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Radian Corp, Austin, TX

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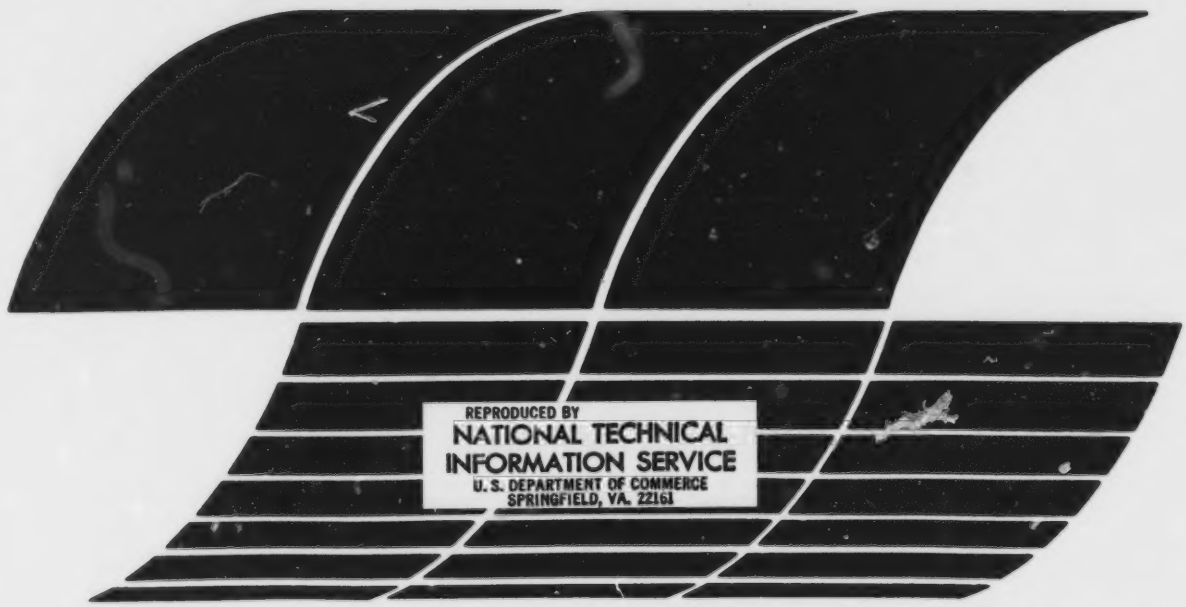

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1.0 INTRODUCTION

To date, government actions aimed at controlling the impacts of ambient nitrogen oxides (NO_x) emissions have focused on combustion modification as the primary basis for the control of both mobile and stationary sources. This approach has been taken because combustion modification is the most cost effective approach to achieving initial reductions in uncontrolled NO_x emissions from all types of combustion sources. Now, however, a number of factors are providing incentives for a reexamination of this basic control philosophy. In particular, recent emission inventories and projections of air quality trends indicate that NO_x emissions from both stationary and mobile sources are increasing. As a result, it appears doubtful that NO_x emission reductions currently attainable by use of combustion modification alone can continue to provide the margin of control necessary to meet either existing or future, more stringent, ambient air quality standards.

One approach which has considerable potential for reducing NO_x emissions beyond the levels currently attainable by combustion modification is flue gas treatment. Whereas combustion modification techniques appear to be capable of reducing combustion source NO_x emissions by approximately 50%, on the order of a 90% reduction in the NO_x concentration of a typical stationary source flue gas is possible with flue gas treatment. The objective of this study which provided the basis for this report was to determine if and when the need will exist for this more stringent level of control.

This report, therefore, analyzes the factors which will determine the level of NO_x control necessary to comply with both existing and future standards. The conclusions of this

analysis as they apply to the need for flue gas treatment technology are presented in Section 2.0. Background information on the nature of the NO_x emission problem including the sources of atmospheric NO_x emissions, the factors which control the transport and conversion of NO_x into a variety of other pollutants, and the ambient levels of NO_x related pollutants is presented in Section 3.0. Section 4.0 addresses the current status of and important trends in NO_x regulations. The factors involved in developing cost effective compliance strategies for NO_x are discussed in Section 5.0. Appendix A contains a description of stationary source flue gas treatment methods.

2.0 SUMMARY AND CONCLUSIONS

The inescapable conclusion of this study is that the need for flue gas treatment as a control technique for nitrogen oxides (NO_x) from stationary combustion sources is not quantifiable at this time. There is no one factor or combination of factors, among those considered, which can be said to demonstrate that any given amount of flue gas treatment is or will be required for attainment or maintenance of present or future standards. This is due to the regionally specific nature of NO_x compliance problems, uncertainties that exist with respect to future NO_x emission reduction requirements for both stationary and mobile sources, and uncertainties surrounding the development and application of NO_x control technologies to coal-fired combustion sources. However, many if not all of the factors analyzed in this study indicate that the number of Air Quality Control Regions with NO_x compliance problems will increase dramatically in the remainder of this century. They further indicate that progressively larger and larger reduction in both stationary and mobile source emissions will be required to attain and maintain compliance in these problem Air Quality Control Regions. The following section summarizes the conclusions resulting from an analysis of the factors which affect whether or not flue gas treatment will be required in the near term future.

NO_x Emission Sources

On a national basis, fossil fuel combustion accounts for greater than 90% of the NO_x emitted from all man-made sources. Overall, these NO_x emissions can be allocated as follows: mobile sources ($\sim$40%) electric utilities ($\sim$25%), other stationary combustion sources ($\sim$30%), industrial processes and other miscellaneous sources ($\sim$5%). However, emission profiles for many Air

Quality Control Regions which are currently experiencing problems with high ambient NO_x levels differ widely from these norms. Examples of both mobile source intensive and stationary source intensive problem areas can be identified. This highlights the regionally specific nature of the NO_x control problem which, in turn, supports the EPA policy of requiring each state to establish regulatory guidelines which are responsive to their localized needs.

Atmospheric Reactions

Most of the NO_x emitted from combustion sources is released as nitric oxide (NO), whereas, nitrogen dioxide (NO_2) is the criteria pollutant which is of concern from an ambient air quality viewpoint. The oxidation of NO to produce NO_2 can occur via a number of pathways. In polluted urban areas, this conversion process appears to be controlled primarily by the reaction of NO with oxidant free radicals. It follows that the maximum impact of a given quantity of stationary source NO_x emissions upon ambient NO_2 levels would be felt in areas having simultaneously high oxidant levels.

Atmospheric Transport

Several recent studies have indicated that NO_x emissions from large stationary sources should not lead to problem ground level concentrations of ambient NO_2 (relative to current standards) on an annual average basis. Achieving compliance with future, more stringent standards (including short term standards) may require the application of FGT, depending on the level of the standard set.

Ambient Concentrations

Although only a few air quality control regions in this country are reporting violations of the current NO_2 National Ambient Air Quality Standard (100 $\mu g/m^3$-annual average), on the order of twenty AQCR's reported ambient NO_2 levels in excess of 80 $\mu g/m^3$ in 1975. Because of this, the growth which is being experienced in all fossil energy consuming sectors may cause ambient NO_2 problems to be experienced in a significant number of new AQCR's in the near-term future.

Standards

Standards which will determine the need for FGT are Federal New Source Performance Standards, New Mobile Source Standards, State Implementation Plan Regulations, National Ambient Air Quality Standards and Prevention of Significant Deterioration requirements. Current Federal New Source Performance Standards are based upon, and therefore require, only the application of combustion modification. Recent health effects studies do not point toward the need for a long-term ambient air quality standard for NO_2 that is more stringent than that which currently exists (100 $\mu g/m^3$-annual average). However, the need for a short-term NO_2 standard was recognized by Congress in the Clean Air Act Amendments of 1977 which require that EPA establish a short-term (1-3 hour average) NO_2 National Ambient Air Quality Standard unless the Administrator deems that this type of standard is not necessary to protect public health. The level of control required to comply with this standard will not be known until the standard is promulgated. However, recent studies by the California Air Resources Board and EPA have indicated that flue gas treatment may not be required in some Air Quality Control Regions if the maximum allowable one hour average NO_2 concentration is

less than 750 $\mu g/m^3$. EPA is currently considering a level somewhere between 200 and 1000 $\mu g/m^3$. California has already established a one hour average standard with 500 $\mu g/m^3$ as the maximum allowable NO_2 concentration.

A number of states and/or air quality control districts have adopted air quality standards which are more stringent than current National Ambient Air Quality Standards for NO_2. Strict enforcement of these standards may create a need for flue gas treatment technology application, particularly in specific problem areas such as California's South Coast Air Basin.

Prevention of Significant Deterioration may require flue gas treatment on stationary sources located in Class I or Class II areas even where New Source Performance Standards and National Ambient Air Quality Standards would not indicate the need.

Control Strategies

Unless a level of control requiring flue gas treatment is adopted by some future New Source Performance Standard or required for Prevention of Significant Deterioration, the question of "if and when" flue gas treatment will be necessary will ultimately be decided in developing State Implementation Plans. Strategies for controlling NO_2 and other NO_x related pollutants are difficult to develop on a national level because each NO_2 problem depends on such area specific factors as topography, meteorology, and emission profiles.

All areas experiencing NO_x compliance problems must attain and maintain compliance by controlling mobile source emissions.

stationary source emissions or both. Emissions from both stationary sources and mobile sources can be reduced either by application of combustion modification or flue gas treatment techniques.

Control Technology

Combustion modification techniques have been developed and commercially applied that are capable of reducing stationary source emissions to 86-260 g/GJ (0.2-0.6 lb/10^6 Btu), depending on the type of fuel burned. Mobile source emissions can be controlled to 0.62-3.7 g/km (1-6 g/mile), depending on the class of vehicle. Flue gas treatment has been commercially applied in Japan for gas- and oil-fired stationary combustion sources and there are numerous programs underway to develop and improve flue gas treatment and combustion modification techniques for coal-fired stationary sources. In addition, post combustion cleanup technology (catalytic converters) capable of reducing emissions to 0.24 g/km (0.4 g/mile) is being developed for mobile sources. The success or failure of these programs will greatly influence the future course of NO_x standards and compliance strategies.

Comparative costs indicate that when a control strategy calls for gross reductions in NO_x emissions from both mobile and stationary sources, the most cost effective control approach involves stationary source combustion modification. Mobile source combustion modification is the next most cost effective NO_x control technique on a cost per ton of NO_x emissions reduced. Stationary source flue gas treatment and finally mobile source flue gas treatment (catalytic converters) are the next most cost effective NO_x control techniques.

Secondary Pollutants

The extent to which ambient oxidant levels are affected by changes in NO_2 concentrations remains to be established. Certainly, recent data indicate that oxidant levels are strongly affected by changes in reactive hydrocarbon emission rates. This finding has provided the basis for a number of oxidant control strategies which are based upon hydrocarbon emission controls. If similar links between ambient NO_2 levels and problem concentrations of secondary pollutants such as peroxyacylnitrates, ozone and atmospheric nitrates are established, this may justify the use of controls which are more effective than conventional combustion modification techniques. Research is currently underway to determine the role of NO_x in the formation of oxidants. Models which relate NO_x emissions rates by source type to ambient levels of NO_2 and other NO_x related pollutants are currently being developed.

Health Effects

Health effects of pollutants are major driving forces behind the development of air quality standards. As such, this area of research is critical to the issue of whether changes are needed in the required levels of NO_x control. Research is ongoing to determine the acute and chronic effects of both short- and long-term exposures to NO_2, oxidants, and nitrates. In addition, studies are underway to determine whether nitrosoamines (known carcinogens) can be formed in the lung from potential precursors such as NH_3 and NO_2 in the ambient air. The results of these studies may indicate the need for flue gas treatment if tighter NO_x control is judged to be necessary to protect human health.

3.0 THE NO_x PROBLEM - SOURCES AND EFFECTS

This section summarizes four key aspects of the nitrogen oxides (NO_x) emission problem. First in Section 3.1, the sources of atmospheric NO_x emissions are identified. The relative significance of the various emission sources and the regional variations observed in NO_x emission profiles are also discussed. The chemistry of atmospheric reactions involving NO_x is briefly reviewed in Section 3.2. This discussion is presented to illustrate why it is necessary to consider more than just ambient NO_2 levels in assessing the possible need for flue gas treatment (FGT) technology. Section 3.3 addresses the considerations involved in assessing the relative impacts of point source NO_x emissions on ground level pollutant concentrations. In Section 3.4 the region-specific nature of the NO_x control problem is highlighted. This is done by considering current air quality trends for regions of the country which are either 1) already out of compliance with respect to ambient NO_2 or oxidant levels or 2) appear to have significant potential for the development of future problems.

3.1 NO_x Emission Sources

NO_x is emitted by both natural and man-made sources. Although natural sources contribute far greater amounts, man-made sources of NO_x are almost entirely responsible for the high ambient NO_x concentrations found in urban and industrialized areas. Combustion of fossil fuels is by far the most significant source of man-made NO_x emissions.

On a worldwide basis, the major source of atmospheric NO_x is biologically produced NO. Globally, natural sources produce about 450 Tg (500×10^6 tons) of NO per year, while technological (man-made) sources emit on the order of 45 Tg (50×10^6

tons) per year of NO_x (including both NO and NO_2) (Reference 1). Estimates indicate that the total emission rate of NO_x from technological sources in the United States is approximately 18-23 Tg (20-25 x 10^6 tons) per year (Reference 2).

While natural source NO_x emissions are much higher on a global scale, they are also fairly evenly distributed. Natural source NO_x emissions contribute a low background concentration as a result. Manmade NO_x, while lower in global mass emissions, can cause localized, high atmospheric concentrations.

3.1.1 Nationwide Emission Trends

U.S. emissions of NO_x from man-made sources for 1970-1976 are estimated in Table 1. As can be seen in the table, the major contributor to technology-associated NO_x in the U.S. is fossil fuel combustion. The combined categories of transportation and stationary fuel combustion contribute about 95% of the total U.S. emissions of man-made NO_x. Stationary source combustion is the single largest contributor, accounting for 51-54% of the total U.S. emissions. The electric utility contribution ranged from an estimated 25% in 1970 to 29% in 1976. By way of comparison, highway transportation emissions increased from 31% in 1970 to 34% in 1976.

Industrial processes, solid wastes (incineration, primarily) and miscellaneous sources are all shown in Table 1 to be minor contributors to the total NO_x emission picture. The potential significance of these sources on a localized basis, however, should not be underestimated. In fact, some of the highest ambient NO_2 levels ever recorded have been measured in eastern Tennessee where high concentrations of nitric acid production and utilization facilities exist.

TABLE 1. NATIONWIDE NO_x EMISSION ESTIMATES
1970-1976 (10^6 metric tons/yr)

Emission Source	Year													
	1970		1971		1972		1973		1974		1975		1976	
Transportation	8.4	(41%)	8.9	(42%)	9.4	(42%)	9.7	(42%)	9.6	(42%)	9.9	(45%)	10.1	(44%)
Highway	6.3	(31%)	6.7	(31%)	7.1	(32%)	7.3	(32%)	7.3	(32%)	7.6	(34%)	7.8	(34%)
Non-highway	2.1	(10%)	2.2	(9%)	2.3	(10%)	2.4	(10%)	2.3	(10%)	2.3	(10%)	2.3	(10%)
Stationary fuel combustion[a]	10.9	(53%)	11.2	(53%)	11.7	(53%)	12.1	(53%)	11.9	(53%)	11.2	(0%)	11.8	(51%)
Electric Utilities	5.1	(25%)	5.4	(25%)	5.9	(27%)	6.3	(28%)	6.2	(27%)	6.1	(27%)	6.6	(29%)
Other	5.8	(28%)	5.8	(27%)	5.8	(26%)	5.8	(25%)	5.7	(5%)	5.1	(23%)	5.2	(23%)
Industrial processes	0.6	(3%)	0.6	(3%)	0.7	(3%)	0.7	(3%)	0.7	(3%)	0.7	(3%)	0.7	(3%)
Chemicals	0.2		0.2		0.3		0.3		0.3		0.3		0.3	
Petroleum refining	0.3		0.3		0.3		0.3		0.3		0.3		0.3	
Mineral products	0.1		0.1		0.1		0.1		0.1		0.1		0.1	
Solid waste	0.3	(1%)	0.3	(1%)	0.2	(1%)	0.2	(1%)	0.2	(1%)	0.2	(1%)	0.1	(1%)
Miscellaneous	0.2	(1%)	0.3	(1%)	0.2	(1%)	0.2	(1%)	0.2	(1%)	0.2	(1%)	0.3	(1%)
Forest wildfires and managed burning	0.1		0.2		0.1		0.1		0.1		0.1		0.2	
Coal refuse burning	0.1		0.1		0.1		0.1		0.1		0.1		0.1	
Total[b]	20.4		21.3		22.2		22.9		22.6		22.2		23.0	

[a] Includes both area and point sources.

[b] Totals may not add due to rounding.

Source: Reference 2.

The increase in total NO_x emissions which occurred during the years 1970-1976 is attributable mainly to an increase in fuel consumed by electric utilities and an increase in highway vehicle travel.

Emission projections are difficult to make because of a variety of unknowns in both emission factors and growth trends. A summary of several recent projections of NO_x emission trends is presented in Table 2. While the bases for these projections vary widely, all of the results indicate very clearly that significant levels of NO_x control will have to be achieved in order to maintain total NO_x emissions at their current levels. A more detailed discussion of how these controls might be implemented is presented in Section 5.0.

3.1.2 Regional Emission Profiles

While the preceding discussion does provide useful insight into the relative significance of the various NO_x emission sources on a nationwide basis, NO_x emission control strategies should be developed on a regional basis. For this reason, data on NO_x emission profiles which are typical of regions of the country which are currently having NO_2 or oxidant compliance problems are considered in this section.

Table 3 lists the ambient air monitoring stations which recorded annual average NO_2 levels in excess of the 100 $\mu g/m^3$ standard in 1975. Also listed are stations which recorded ambient NO_2 levels greater than 80% of the standard.

The relative contributions of the various NO_x emission sources located within each of these problem Air Quality Control Regions (AQCR's) are shown in Table 4. An obvious observation

TABLE 2. SUMMARY OF NO_x EMISSION TRENDS PROJECTIONS

Source and Year	Basis for Projection	Significant Results	Conclusions/Comments
Interagency Committee - 1977 (Ref. 3-3)	National increases modelled. Base year 1970 Emission factor ratios for stationary sources 0.9 for 1980, 0.7 for 1990, 0.5 for 1999. Sources, 2% growth for mobile sources Mobile Source Standards - several different scenarios including one for current standards. Emission factor ratios for mobile sector 0.73 for 1980, 0.53 for 1990, and 0.52 for 1999. Vehicle turnover rate 13 years for LDV.	Relative to 1970 levels, and with current standards, NO_2 concentrations in the air will be 4% higher in 1980, 3% higher in 1990, and 8% higher in 2000.	Achieving the assumed stationary source emission factor ratios would require widespread application of controls (including FGT). The growth rates assumed are critical and are judged to be too low, indicating even more need for controls.
Greenfield, Attaway, and Tyler - 1977 (Ref. 3-4)	Twenty problem AQCR's modelled. Base year 1975 for utilities and transportation; 1973 for other sectors. 5-6% growth in electrical generation. Four fuel use scenarios - Maximum coal, high coal - low nuclear; nominal growth; low coal - high nuclear. Three emissions restrictions scenarios- The most stringent of emission restrictions (either state or federal), BACT applied to all sources, projected NSPS. Mobile source emission factors for LDV- low altitude 1g/mile in 1985 and 0.4g/mile in 2000; high altitude 0.97 g/mile in 1985 and 0.4 g/mile in 2000; California 0.85 g/mile in 1985 and 0.4g/mile in 2000. Mobile source emissions based on average per capita ownership projections. Turn over rates for power plants taken into account.	In 1985 6 AQCR's are predicted to be out of compliance under all emissions restrictions. By 2000 10 AQCR's are projected exceeding the standard under low coal, most stringent emissions restriction scenario; 19 AQCR's are projected to be out of compliance under the maximum coal, least stringent emission restrictions.	There are a few AQCR's which will require all available control methods to stay in compliance (including FGT).

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TABLE 2. SUMMARY OF NO_x EMISSION TRENDS PROJECTIONS (Continued)

Source and Year	Basis for Projection	Significant Results	Conclusions/Comments
Acurex Corporation/ Aerothermal Division- 1977 (Ref. 3-5)	Chicago and Los Angeles modelled. Base year concentrations 132 $\mu g/m^3$ 160 $\mu g/m^3$ for Los Angeles; 96 $\mu g/m^3$ and 120 $\mu g/m^3$ for Chicago. Three growth scenarios - nominal growth, low mobile, and high stationary. Nominal growth assumes moderate growth for stationary sources, 1 g/mile mobile standard beyond 1980. Low mobile scenario assumes 0.4 g/mile mobile standard beyond 1981. Source weighting factors used to show sensitivity to stack height.	Except for low mobile growth cases, maximum control of stationary sources needed for all cases in 2000 in Los Angeles. It would also be needed for the concentrations predicted by 1985 based on the high base year. In Chicago, control of stationary sources is required in all cases except for 1985 if the low base year is used. For both cities in 2000, all combustion modification technology will be required and ammonia injection will be required in some cases.	The control level required in both cities is dominated by mobile source control assumptions. The low mobile scenario seems unrealistic. FGT will be needed by 2000 in these cities and possibly in 1985 under some conditions.
Argonne Labs, TRC - 1976 (Ref. 3-6)	National Emissions modelled. 1975 base year. General scenarios for applying NSPS at different rates. Mobile source emissions assumed to be 0.4 g/mile beginning in 1978.	Under present control levels emissions will increase 66% by 1985. If BACT is applied to all new sources, the increase will be 24%. Only a few stationary sources are capable of significant quantities of emission control. Total emissions will increase through 1990 in spite of the most rapid application of NSPS. Stationary source control cannot compensate for mobile source growth.	The results indicate the need for further development of control technologies such as FGT, so that more stringent NSPS could be applied.
Interagency Committee- 1976 (Ref. 3-7)	National emissions modelled. 1972 base year. Mobile source growth rate 3%. Emission factor ratios given for several mobile standards. For current standard, emission factor ratios are 0.69 for 1980, 0.30 for 1990, 0.29 for 1999. Stationary source growth rate 3.9%. Emission factor ratios for stationary sources 0.90 for 1980, 0.70 for 1990, 0.40 for 1999. A 13 yr turnover rate assumed for mobile sources.	Predictions are for 12-17 of AQCR's to be out of compliance by 1980. Increase in NO_x emissions will average 12-24%.	Emission factor ratios used imply stringent control methods for stationary sources, including FGT by 1999. The assumed growth rates are thought too low.

Source: References 3, 4, 5, 6, 7.

TABLE 3. AQCR'S INDICATED AS POTENTIAL NO_2 PROBLEM AREAS BY 1975 MONITORING DATA

AQCR #	Monitoring site reporting highest annual average	Annual average ($\mu g/m^3$)
207	Kingsport, Tennessee	186
24	Pasadena, California	153
67	Chicago, Illinois	111
43	New York, New York	102
119	Boston, Massachusetts	102
42	Springfield, Massachusetts	100
45	Philadelphia, Pennsylvania	98
36	Denver, Colorado	96
226	Vinton, Virginia	96
70	St. Louis, Missouri	94
123	Southfield, Michigan	94
47	Seven Corners, Virginia	88
15	Phoenix, Arizona	85
18	Memphis, Tennessee	85
103	Ashland, Kentucky	85
78	Louisville, Kentucky	84
131	Minneapolis, Minnesota	84
174	Cleveland, Ohio	84
79	Cincinnati, Ohio	82
229	Seattle, Washington	82

Source: Reference 8.

TABLE 4. CONTRIBUTIONS OF THE VARIOUS SECTORS TO 1975 NO_x EMISSIONS IN PROBLEM AQCR'S[a]

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AQCR Number	AQCR Location	Electrical Utilities (% of Total)	Industrial[b] (% of Total)	Commercial (% of Total)	Residential (% of Total)	Transportation (% of Total)	Misc. (% of Total)	Total (tons NO_2)	Maximum annual ave. NO_2 conc. ($\mu g/m^3$)[c]
207	Kingsport, Tennessee	45	17	1.8	0.9	12	1.6	217,000	186
24	Pasadena, California	11	11	3.1	2.6	60	10	730,000	154
67	Chicago, Illinois	24	29	3.9	1.1	36	6.1	685,000	111
43	New York, New York	11	6.4	9.9	4.0	63	5.8	1,330,000	107
119	Boston, Massachusetts	10	7.0	12	2.9	64	1.5	280,000	102
42	Springfield, Massachusetts	12	13	7.4	4.2	59	4.1	141,000	100
45	Philadelphia, Pennsylvania	12.6	20	4.6	3.0	54	5.7	489,000	98
36	Denver, Colorado	30	8.1	3.2	2.6	47	9.1	135,000	96
226	Vinton, Virginia	8.5	42	3.3	1.9	39	6.0	75,000	96
70	St. Louis, Missouri	41	16	2.6	2.1	35	3.3	261,000	94
123	Southfield, Michigan	21	17	4.3	3.5	41	13	403,000	94
47	Seven Corners, Virginia	23	2.5	9.8	3.2	56	5.7	186,000	88
15	Phoenix, Arizona	8.5	4.9	1.9	1.8	67	16	108,000	85
18	Memphis, Tennessee	47	8.4	2.4	1.8	36	4	94,000	85
103	Ashland, Kentucky	75	6.5	0.9	0.8	15	1.6	190,000	85
78	Louisville, Kentucky	41	16	3.0	1.9	33	2.2	114,000	84
111	Minneapolis, Minnesota	29	9.1	3.6	2.7	51	4.7	165,000	84
174	Cleveland, Ohio	25	25	3.8	2.1	39	4.2	331,000	84
79	Cincinnati, Ohio	27	18	4.9	3.2	43	4.2	146,000	82
229	Seattle, Washington	-	46	2.9	1.7	39	9.9	200,000	82
Total U.S.[d]	28%		e	e	e	44%	e	24,200,000	-

[a] Source: Reference 4.
[b] Includes combustion and process emissions.
[c] From Table 3-5.
[d] From Table 3-1.
[e] Commercial and Residential and Misc. = 28%.

which can be made from these data is the fact that there is no "typical" problem AQCR emission profile. About half of the AQCR's listed have higher NO_x emissions from the transportation sector than the U.S. average contribution of 44%. There is also considerable variation in the electric utility contributions listed. In two of the AQCR's, electric utility sources contributed only 8.5% of the total emissions of NO_x. The maximum utility sector contribution seen in Table 4 was 75% (AQCR 103 - Ashland, KY). Seven of the 20 AQCR's listed had higher NO_x emissions from the utility sector than the U.S. average of 28%.

These data clearly indicate the site specificity of the NO_x emission problem. Unfavorable meteorological conditions coupled with high NO_x emissions from any one of a number of potential sources can create NO_2 compliance problems. These trends illustrate why compliance strategies for the attainment of ambient air quality standards should be developed on a regional basis.

Another factor which is not reflected in the data shown in Table 4 but which should be considered in this assessment is the impact of seasonal variations in fuel consumption and therefore, NO_x emission profiles.

3.1.3 Long-Term Trends in NO_x Emission Profiles

The hazards of forecasting the effects of technological and economic changes are well known. If future air quality standards are to be attained, however, general growth trends must be recognized and considered in planning recommendations.

There are several current trends which will undoubtedly impact the relative significance of large point sources as NO_x emitters. Some of these trends include:

- in the short-term, an increase in the use of coal, primarily in the electric utility and industrial sectors,

- an increase in the degree of electrification, primarily in the residential and commercial sectors,

- a decrease in natural gas consumption in all sectors, and

- a decrease in the NO_x emissions from mobile sources as older cars are replaced with newer models having lower emissions.

Some of these effects will be offset by trends such as

- an increase in the use of nuclear and solar energy, and

- an increase in the application of NO_x control techniques to existing sources and the replacement of old "dirty" units with new ones.

In addition, the overall energy use picture is clouded by the uncertain effects of future conservation measures such as:

- decreased residential/commercial energy usage for heating, cooling, lighting, etc., and

- energy recovery schemes (*e.g.*, combustion air preheating) which will continue to be widely applied in the industrial sector.

The net effects of these trends are difficult to predict, primarily because of the uncertainties which exist in the projected growth rates of the various energy consuming sectors. It is expected, however, that the significance of large point sources as NO_x emitters will increase.

3.2 Atmospheric Reactions Involving NO_x

NO_x emitted from both stationary and mobile sources (mainly in the form of NO) may undergo considerable transformation while being transported from an emission source to a sink and/or receptor. In particular, the chemical reactions which result in the formation of urban smog are very relevant to the NO_x emission problem.

The role of NO_x in urban smog formation is very complex. Although much work has been done recently to develop a better understanding of the mechanisms involved in the formation of various atmospheric pollutants, considerable work remains to be done, particularly in the areas listed below.

- quantification of the various reactive chemical species present in urban air masses, and particularly the reactive intermediates which participate in rate controlling steps for key component formation reactions

- identification of the specific chemical mechanism(s) whereby important chemical species are formed

- quantification of important variables which affect the rates of formation and disappearance of important chemical species

Much information of this nature has been developed, primarily in "smog chamber" studies using synthetic mixtures of polluted air. Because of several obvious problems, all of this work may not be directly applicable to "real world" situations. It is true, however, that this work has led to a good understanding of many of the important reactions involved in the formation of urban smog.

Researchers are currently applying this information in the development of a variety of air quality simulation models. Hopefully, these models will be capable of relating emissions to air quality, taking into account meteorological variables, photochemical reactions, and pollutant transport. A model which accurately predicts the levels of all significant pollutants at their points of maximum impact is the ultimate goal. It should be able to predict air quality in the vicinity of the emissions, as well as in adjacent areas and should be applicable to any area. Such a model would serve as a vital tool for developing control strategies. No such model is available currently. A good description of the various types of models and their status of development may be found in Reference 9.

The role of NO_x in the formation of photochemical smog is briefly summarized below. This discussion is presented to illustrate the fact that the potential impacts of atmospheric NO_x emissions cannot be assessed only in terms of their effects upon ambient NO_2 levels. For a more comprehensive discussion of this subject, the reader should refer to the recent reviews found in References 10 through 14.

As discussed previously, the bulk of the NO_x emitted from combustion sources is released in the form of nitric oxide, NO. Since the conversion of NO to NO_2 is a critical first step

in the sequence of reactions leading to the buildup of high concentrations of NO_2 as well as other pollutants, this reaction will be discussed first.

NO may react with molecular oxygen according to Reaction 1 to form NO_2.

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

However, the rate of this reaction is not sufficient to account for the rapid conversion of NO to NO_2 which is observed in polluted urban atmospheres. The key to this overall conversion of NO to NO_2 is now considered to be the reaction of NO with peroxy free radicals. In particular, the hydroperoxy radical is felt to be an important species

$$HO_2 + NO \rightarrow NO_2 + OH\ ; \qquad (2)$$

although, alkylperoxy

$$RO_2 + NO \rightarrow RO + OH \qquad (3)$$

and acylperoxy

$$RC(=O)-O_2 + NO \rightarrow RC(=O)O + NO_2 \qquad (4)$$

radicals can also participate in NO oxidation reactions. Acylperoxy radicals can also react with NO_2 to form peroxyacyl nitrates (PAN), an important class of eye irritants.

A variety of paths exist for the formation of these highly reactive intermediates. Hydroxyl radicals and CO for example can react to form hydroperoxy radicals according to the following sequence:

$$OH + CO \rightarrow H + CO_2 \quad (5)$$

$$H + O_2 + M \rightarrow HO_2 + M, \quad (6)$$

where M is a third body capable of absorbing excess vibrational energy. Hydroxyl radicals also can react with a variety of hydrocarbons (such as aldehydes) to produce hydroperoxy radicals.

Ozone formation via NO_2 photolysis provides another important mechanism whereby a number of important species are formed.

$$NO_2 + \text{sunlight (2900-4300A)} \rightarrow O^* + NO \quad (7)$$

$$M + O^* + O_2 \rightarrow O_3 + M \quad (8)$$

In these equations, O* is an activated oxygen atom and M is any third body which is capable of absorbing the excess energy released in reaction 8.

The ozone thus formed may react with a variety of atmospheric pollutants. Among them are NO and NO_2.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (9)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (10)$$

This last reaction is important because of the subsequent possibility of NO_3 reaction with other species such as NO_2 and H_2O to form nitric acid thus providing a mechanism for NO_2 removal from the atmosphere. Ozone can also react with the hydrocarbons present in the air to form a wide range of reactive species or undergo photolysis,

$$O_3 + \text{sunlight} \rightarrow O^* + O_2, \qquad (11)$$

to form an activated oxygen atom which can subsequently participate in important photochemical reactions such as hydroxyl radical formation,

$$O^* + H_2O \rightarrow 2OH, \qquad (12)$$

or hydrocarbon oxidation.

In addition to the gas phase pollutants described above, smoggy urban air contains aerosols and particulates which cause light dispersion and haze. Much work has been done in analyzing data from the Los Angeles Basin area concerning secondary aerosol and particulate formation and characterization. It has been shown that secondary aerosols (sulfates, nitrates, and organics) can be formed by reactions involving primary gaseous pollutants (SO_2, NO_x, and hydrocarbons) (Reference 15). It has been further shown that under some circumstances aerosol formation from gas-to-particulate conversions may equal or exceed that due to primary emissions (Reference 16).

When organic compounds are broken up into smaller more reactive fragments as a result of atmospheric reactions, these fragments may polymerize into higher molecular weight compounds which can condense to form aerosol droplets. Sulfate aerosols and particulates, can result from the nucleation and hydration of sulfuric acid in the atmosphere (Reference 17). The formation of nitrate particulates and aerosols is more complex, however. The photochemically produced precursor of atmospheric nitrates is nitric acid, HNO_3, which has a relatively high volatility at trace concentrations. As a result, HNO_3 does not tend to condense as sulfuric acid does. Rather, HNO_3 must react with other

species or dissolve in a condensed phase already present. One obvious possibility is the reaction of HNO_3 with NH_3 to produce ammonium nitrate.

$$NH_3 + HNO_3 \rightarrow NH_4NO_{3(s)} \qquad (13)$$

Nitrate particulates do, in fact, appear to exist primarily as ammonium salts (Reference 15); although, the existence of this reaction as a significant mechanism in the atmosphere remains to be confirmed.

Many gaseous nitrogen species such as NO_2, N_2O_5 and HNO_3 can dissolve and/or react in an aqueous phase, but the role of these reactions in atmospheric aerosol formation remains to be established (Reference 18).

The reactions discussed to this point are only elementary examples of the incredibly complex series of reactions which occur in sunlight irradiated atmospheres. Ultimately, these reactions result in the conversion of NO into other substances which must subsequently be removed from the air by adsorption or absorption.

The existence of the chemical reactions which were just described means that the control of NO_x may have to be considered in developing effective control strategies for both ambient oxidants and particulates. Whether these considerations will require more stringent levels of NO_x control that those currently required to satisfy ambient NO_2 standards remains to be established. To date, no oxidant- or particulate-related NO_x emission controls have been promulgated (Reference 19).

Recent studies of this subject have shown that the significance of NO_x as a precursor for the formation of other pollutants appears to be dependent not only on the $HC:NO_x$ ratio, but also on the transport mechanisms which determine how long a given pollutant mix remains in the air. A study by Trijonis (Reference 20), comparing changes in air quality to changes in emissions in Southern California, indicates that this is so, at least for Southern California. A decrease in the $HC:NO_x$ emission ratio in the western portion of the South Coast Air Basin caused by reducing HC emissions while allowing NO_x emissions to rise has resulted in decreased oxidant levels in western and central Los Angeles County but increased oxidant levels in the eastern South Coast Air Basin. This finding along with indications that large stationary sources located in the western part of the basin may be contributing to high NO_2 levels in the eastern portions supports the conclusion that NO_x emission controls should be incorporated into the oxidant control strategy for the South Coast Air Basin.

The problems associated with devising oxidant control strategies are becoming more and more complex. It has been recognized that oxidant problems in outlying areas may be caused by the transport of air parcels from urban or industrialized areas (References 19 and 21). It is also thought that the age of the pollutant mix (length of time in the air) affects the atmospheric chemistry and, therefore, the severity of the oxidant problem. For these reasons, control strategies for urban, suburban, industrial, and rural areas cannot be dissociated. Oxidant control strategies developed for a specific area should, therefore, address not only local emissions, but also existing background levels of key pollutants (Reference 19). All of the factors which influence the levels of ambient oxidants (length of time pollutants remain in the air, distance of pollutant transport, sources of natural emissions, etc.) are very area-specific and

will demand the development of a control strategy which is tailored to the specific requirements of the area.

In addition to the documented role of NO_x in oxidant formation, it has been suggested that nitrosoamines could be formed in the atmosphere through the reaction of NO_2 and amines. This hypothesis generated much concern because of animal tests which show nitrosoamines to be powerful carcinogens.

The reaction of NO_2 and amines has been observed in the lab under acid conditions. The presence of ozone has further been shown to accelerate nitrosoamine formation. In theory, the reaction should proceed in the atmosphere. To date, however, there have been no monitoring data collected to support the hypothesis of nitrosoamine formation in the atmosphere. All nitrosoamines detected in air have been traced to specific point source emissions (References 22 and 23). Inhalation of precursors has also been suggested as a possible mechanism leading to nitrosoamine synthesis in the lung. This mechanism is not thought to be significant, however (Reference 22).

Confirmation of the atmospheric formation of nitrosoamines or of nitrosoamine formation in the lung could eventually provide a basis for stringent NO_x controls. Monitoring work in this area is continuing at EPA, the National Institute for Occupational Safety and Health, and at the University of California.

3.3 Atmospheric Transport of NO_x

Stationary point sources are emission sources which can be approximated by single points as opposed to area sources which are characterized by a fairly uniform distribution of emissions over a broad area. In order to assess the impacts of NO_x emissions from large stationary point sources upon the concentrations

of NO_x-related pollutants at ground level, the factors which relate to the physical transport of large point source plumes need to be considered. In addressing this problem, two limiting cases can be proposed.

The first involves a situation such as that which frequently occurs during periods of air stagnation in the South Coast Air Basin (Los Angeles area) in Southern California. In this situation, it is probably reasonable to allocate ambient NO_x levels to the various source categories in proportion to the emission rates of NO_x from those sources. However, the need to handle mobile source NO_x emission spikes (caused by peak traffic periods) must be recognized.

The second case, which is more commonly encountered, involves the impact of stationary source plumes at points which are downwind from the emission source. The considerations in this case are the factors which affect the ambient levels of NO_x related pollutants in the vicinity of a ground level receptor.

The effects of emissions from large stationary sources on air quality depend not only on the chemical phenomena which were discussed in the previous section, but also on physical transport of the plume. The behavior of a plume from a large stationary source can be considerably modified by meteorological parameters such as cloud cover, wind patterns, temperature and relative humidity which result in part from spatial differences in the earth's ability to absorb and reradiate the energy received from the sun. In addition, the ability of the atmosphere to mix and dilute pollutants is highly dependent not only on temperature, but also on the spatial variability of temperature, particularly in the vertical direction. Local topographical features have the effect of modifying large-scale weather patterns

which control pollutant transport over large (regional) areas. In particular, topography can also influence the wind patterns which govern the dispersion of pollutants in the atmospheric boundary layer.

The important meteorological variables which affect the transport and dispersion of pollutants from large elevated point sources include wind speed, wind direction and wind direction variability, and vertical temperature structure (stability and mixing depth).

The effect of an increase in wind speed is to increase the degree of mixing of the dispersing material in the horizontal downwind direction. In addition, the rise of the plume from the source is diminished with increasing wind speed.

Spatial and temporal variations in the wind direction affect not only the general direction of pollutant transport, but also the horizontal dilution of the plume. During periods of fairly persistent spatial and temporal wind directions, plumes from large elevated point sources may be identified up to 500-1000 kg (310-620 miles) downwind (Reference 24). However, during periods of fluctuation in the wind direction the horizontal crosswind dispersion of the plume is enhanced and maximum downwind concentratior may drop off rapidly with distance.

The temperature structure of stability of the atmosphere also defines the dispersive capability in the vertical and horizontal crosswind directions. As the atmosphere becomes more stable, plumes emitted from large elevated point sources assume a relatively compact shape. However, as the air becomes less stable, plume spread in the vertical and horizontal crosswind direction increases.

Highest ground level concentrations in the vicinity of large stationary point sources occur during conditions which tend to minimize lateral, vertical, and downwind dispersion while at the same time allowing the plume to reach ground level. For low-level area sources or "urban"-type sources, maximum ambient NO_x concentrations very near the source occur during stable, nighttime, light wind conditions. However, because these same conditions cause emissions from elevated point sources to be confined to elevated stable layers, they do not give rise to high ground level concentrations for these types of emissions.

Two conditions recognized for producing adverse dispersion conditions for large elevated point sources are limited mixing and coning (Reference 25). The limited mixing or trapping condition is most often associated with the presence of a large slowly moving high pressure system approximately centered over the area. At night, a strong ground based inversion develops beneath an overlying stable layer, and emissions from a large elevated point source become embedded in this stable layer and do not reach the ground. During the midmorning, ground based turbulent mixing reaches the base of the plume, dispersing it rapidly to the ground with resultant high peak concentrations (up to about 30 minutes duration). If the mixing depth continues to develop slowly beneath the overlying stable layer, relatively high ground level concentrations may persist for several hours.

During periods of limited mixing, high ground level concentrations are also associated with low wind speeds and the resultant decrease in horizontal downwind dispersion. However, if the wind speeds are too low, considerable meander in the plume may occur due to wind direction variability, and ground level concentrations will drop.

The phenomenon of coning, *i.e.*, plume dispersion during periods of near neutral stabilities and moderate-to-strong winds, gives rise to relatively high concentrations although short-term coning concentrations are typically not as high as short-term limited mixing concentrations for large, elevated point sources. The magnitude of coning concentrations is very sensitive to the wind speed. If the speed is low the plume rise will be large and ground level concentrations will be diminished. In addition, for low wind speeds, plume meander may increase and resultant pollutant concentrations, especially for longer averaging times (3-24 hours), may decrease. If the wind speed is high, the horizontal dilution of the plume will increase and ground level concentrations will drop.

Often the highest ground level concentrations occur at great distances from large, elevated point sources during coning periods, because during such conditions, wind direction variability (temporal and spatial) is often minimized. As a result the point of maximum plume impact may remain near the same location for long periods of time (up to 24 hours). This type of plume behavior may impact the required controls for meeting a short term standard.

The interaction between complex terrain and emissions from large point sources can influence ground level concentration patterns. The increased roughness of the ground surface in areas of complex terrain may generate additional turbulence and enhance plume dilution. Topographical features such as narrow valleys or elongated bluffs can induce channeling of the plume, limiting its spread in the horizontal crosswind direction. In addition, the vertical temperature structure within narrow valleys may be such that the mixing layer may not develop as rapidly as it does over flat terrain. As a result, periods of limited mixing may be more severe, especially for low-level point source releases.

The impingement of plumes from elevated point sources against elevated terrain can often result in very high ground level concentrations (Reference 26). For periods during which the plume is embedded in a stable layer and the wind direction is fairly persistent, the plume may travel for great distances (>25 km) before impinging against vertical terrain features. After traveling these distances, ground level concentrations may be relatively high because of the limited vertical and horizontal crosswind dispersion of the plume.

The transport phenomena and dispersion associated with large point sources differ from those for low-level area sources in several ways which are summarized below.

- Peak ground level concentrations occur closer to the source for area sources and farther downwind for large point sources. This observation is a reflection of the difference in the heights of the plumes.

- Because of the larger horizontal crosswind extent of area sources and because the source density is often fairly homogeneous through the area, peak ground level concentrations resulting from area sources often cover a large area. On the other hand, the point of maximum impact for point sources usually covers a small area.

- For large area sources, peak concentrations are mainly a function of the wind speed and the magnitude and extent of the vertical dispersion. Because of their large horizontal dimensions, the effect of horizontal crosswind dispersion

is minimized in comparison to the effect of horizontal crosswind dispersion on point source emissions.

- Highest ground level concentrations associated with emissions from large point sources typically occur during periods of limited layer mixing and coning. Highest levels resulting from low-level area source emissions typically occur during periods of light winds, stable conditions and low-mixing depths.

Consideration of transport processes and plume behavior not only indicates another difficult complexity affecting air quality, but also shows some of the reasons that pollution problems may exist in certain regions and not in others. The discussion above emphasizes the fact that meteorological and geographical conditions determine the location of impact of a plume and its degree of dispersion. If conditions exist which are conducive to worst-case behavior described in this section, stringent controls on large sources of NO_x may be indicated, even as stringent as FGT, depending on the severity of the problem.

Another facet to the problem of plume transport is the fact that a plume may travel for long distances, creating a longer reaction time for gases, aerosols, and particulates in the mixture. Because the age of a pollutant mixture is an important factor in both $NO \rightarrow NO_2$ conversion and oxidant formation, plumes from large stationary sources can contribute to oxidant problems downwind of the source. Confirmation of this phenomenon could give greater impetus to stringent controls for NO_x which could potentially include FGT if site specific oxidant problems were severe enough.

3.4 Air Quality

Because of transport phenomena and physical and chemical transformation processes occurring in the atmosphere, NO_x emissions are not directly relatable to the levels of NO_2 measured in the atmosphere. Most nitrogen oxides are emitted as NO, changing rapidly in the atmosphere until an equilibrium between NO and NO_2 is established. Most monitoring data are collected for NO_2, the criteria pollutant. Thus, while emissions are measured in terms of nitrogen oxides (NO_x), air quality is measured in terms of NO_2 concentration. In this section, the levels of NO_2 and oxidants found in the atmosphere in air quality problem areas in the U.S. are discussed.

Nitrogen oxides are not evenly distributed globally. Urban and industrial areas have much higher atmospheric concentrations than nonurban areas. Background levels are very difficult to determine; however, concentrations estimated from several sources are presented in Table 5.

TABLE 5. MEAN BACKGROUND LEVELS OF NITROGEN OXIDES

NO	2.5 $\mu g/m^3$ (2 ppb) land areas between 65°N and 65°S 0.25 $\mu g/m^3$ (0.2 ppb) all other areas
NO_2	7.5 $\mu g/m^3$ (4 ppb) land areas between 65°N and 65°S 0.94 $\mu g/m^3$ (0.5 ppb) all other areas

Source: Reference 1.

Concentrations of NO_2 measured in urban and industrial areas may reach levels several hundred times higher than the background levels presented here.

Levels of NO_2 in the atmosphere vary with time as well as with geographical location. Diurnal variations are typical, due in large part to cycles in human activity. Vehicular traffic is a notable cause of increased NO_2 levels. During low traffic periods, the NO_2 may be dispersed or converted, thereby reducing the concentrations. Seasonal patterns which must also be considered are caused by variations in the temperature, prevailing winds, and solar radiation intensity, as well as by variations in the amount of heating fuel combusted.

A number of areas in the United States are experiencing high atmospheric levels of NO_2 and photochemical oxidants. Table 6 summarizes the number of AQCR's reporting NO_2 and oxidant standard violations for the years 1970-1974. Of the 247 total AQCR's only 4 were exceeding the NO_2 annual average standard at that time, but the oxidant standard was being exceeded in 76 AQCR's. Even though only a few AQCR's were actually exceeding the NO_2 standard, a study of 1975 monitoring data resulted in a list of 20 AQCR's containing 30 percent of the U.S. population which have potential NO_2 problems. This list was shown in Table 3.

TABLE 6. NUMBER OF AQCR'S REPORTING NO_2 AND OXIDANT LEVELS IN EXCESS OF STANDARDS

Oxidant	1970	1971	1972	1973	1974
AQCR's reporting at[a] least minimal data	17	30	51	77	86
1-hour standard exceeded	14	24	31	65	76
Nitrogen dioxide AQCR's reporting at least one station-yr.	11	12	15	28	101
Annual standard exceeded	2	3	2	4	4

[a]Minimal data consists of at least 3-24 hour samples or 400 hourly values.

Source: Reference 2.

A list of potential NO_2 problem areas compiled from 1974 monitoring data contained a few AQCR's which did not appear as problem areas in the list contained in Table 4. They are San Diego (#29), San Francisco (#30), Atlanta (#56), Baltimore (#115), McLean-Mercer-Oliver Co. (#172), Canton-Cleveland (#174), Salt Lake City (#220), and Richmond (#225) (Reference 2). If these AQCR's are considered to remain potential problem areas and added to the list of 20 shown in Table 4, a total of 28 of the 247 areas might have an NO_2 problem now or in the near future.

A list of AQCR's in which oxidant levels were exceeding the one-hour standard in 1973 and 1974 is included in Table 7. Although control strategies for photochemical oxidants do not include NO_x emission limitations at this time, this is a possibility for future control strategies.

These air monitoring data clearly show that the control of NO_2 and oxidants is an urban problem. High levels of these pollutants are not being measured uniformly throughout the United States. Comparatively, the oxidant problem appears much worse than the NO_2 problem; 1974 data show that oxidant levels were exceeding the air quality standard in 76 AQCR's, but NO_2 levels were exceeding the standard in only 4 AQCR's.

Left unchecked, the numbers of AQCR's out of compliance with respect to NO_2 would be expected to increase with growth, however. An EPA study predicts that 12-17 AQCR's will be exceeding the current NO_2 standard by 1980 (Reference 7). Such estimates emphasize the importance of including growth projections in control strategies and also point to the fact that the problem of high levels of pollutants may become more prevalent in the future.

TABLE 7. AQCR'S EXPERIENCING VIOLATIONS OF THE ONE-HOUR NAAQS FOR OXIDANTS DURING 1973, 1974, and 1975

AQCR		1973 As of 4/7/75 2nd high $\mu g/m^3$	1974 Partial year 2nd high $\mu g/m^3$	1975 2nd high $\mu g/m^3$
004	Birmingham	435	280	269
005	Mobile	206	280	245
007	Huntsville	-	-	196
013	Las Vegas	438	300	200
015	Phoenix - Tuscon	372	-	255
018	Memphis	196	240	255
024	Los Angeles	1156	660	784
025	N. Central Coast	293	210	216
028	Sacramento Valley	431	170	412
029	San Diego	587	340	372
030	San Francisco	509	170	392
031	San Joaquin Valley	509	230	372
032	S. Cent. Coast. Cal.	254	170	216
033	S.E. Desert, Cal.	548	600	372
036	Denver	548	500	349
043	Metro New York	456	350	510
045	Philadelphia	744	720	625
047	Washington, D.C.	744	300	451
049	Jacksonville	-	-	451
050	S.E. Florida	270	-	196
051	S.W. Florida	215	-	-
052	West Central Florida	-	-	274
055	Chattanooga	-	-	427
056	Atlanta	195	10	324
060	Hawaii	166	-	-
067	Chicago	568	810	427
069	Metropolitan Quad Cities	-	-	210
070	St. Louis	764	500	862
072	Paudcah, Ky.	101	200	204
075	Springfield, Ill.	-	225	-
077	Owensboro, Ky.	-	200	214
078	Louisville	362	200	461
079	Cincinnati	333	310	412
080	Indianapolis	225	330	245
085	Omaha	205	180	225
086	Sioux City	-	-	173
088	Northeast Iowa	-	-	176
092	S. Cent. Iowa	225	500	196
094	Kansas City	-	-	160
095	Topeka	190	-	200
099	S. Cent. Kansas	170	460	560

(Continued)

TABLE 7. AQCR'S EXPERIENCING VIOLATIONS OF THE ONE-HOUR NAAQS FOR OXIDANTS DURING 1973, 1974, and 1975 (Continued)

AQCR		1973 As of 4/7/75 2nd high $\mu g/m^3$	1974 Partial year 2nd high $\mu g/m^3$	1975 2nd high $\mu g/m^3$
102	Lexington	-	-	231
103	Ashland, Ky.	146	370	-
106	S. La. - S.E. Texas	636	390	369
107	Berlin, N.H.	195	110	127
115	Baltimore	450	-	372
117	Pittsfield, Mass.	-	310	323
118	Worchester	-	350	308
119	Boston	409	400	376
120	Providence	274	410	329
121	Nashua, N.H.	194	230	247
122	Central Michigan	-	-	372
123	Detroit	208	180	514
124	Toledo	235	-	265
127	Central Minnesota	-	-	343
128	S.E. Minnesota	-	-	333
129	Duluth	-	-	274
131	Minn. - St. Paul	186	130	231
151	Scranton	-	500	482
152	Albuquerque	244	180	245
153	El Paso	-	160	321
158	Syracuse	344	250	225
159	Glen falls, N.Y.	233	220	194
160	Rochester	231	170	-
161	Schenectady	356	270	284
162	Buffalo	280	270	404
164	Elmira	-	-	263
167	Charlottee, N.C.	288	220	320
171	Asheville, N.C.	210	210	120
173	Dayton	245	160	250
174	Cleveland	352	130	451
176	Columbus	274	90	306
178	N.W. Penn. - Youngstown	313	130	496
181	Steubenville	-	-	343
184	Okla. City	400	310	239
186	Tulsa	176	160	190
193	Portland (Ore.-Wash.)	246	260	294
195	Cent. Pennsylvania	-	250	325
196	S. Cent. Pennsylvania	-	380	370
197	S.W. Pennsylvania	-	180	416
200	Columbia, S.C.	155	280	245

(Continued)

TABLE 7. AQCR'S EXPERIENCING VIOLATIONS OF THE ONE-HOUR NAAQS FOR OXIDANTS DURING 1973, 1974, and 1975 (Continued)

AQCR		1973 As of 4/7/75 2nd high $\mu g/m^3$	1974 Partial year 2nd high $\mu g/m^3$	1975 2nd high $\mu g/m^3$
207	E. Tenn. - S.W. Virginia	568	230	323
208	Mid-Tennessee	205	340	392
212	Austin-Waco	313	230	206
214	Corpus Christi	219	250	241
215	Dallas	248	290	323
216	Houston	484	340	588
217	San Antonio	-	170	296
220	Salt Lake City	217	240	296
223	Hampton Roads	215	350	251
225	Richmond	245	270	353
229	Puget Sound	78	260	235
239	S.E. Wisconsin	450	230	425
240	S. Wisconsin	211	130	-

Source: References 7, 27.

4.0 CURRENT NO_x REGULATIONS AND TRENDS IN NO_x LEGISLATION

The need to utilize FGT technology to control NO_x emissions from large stationary point sources will depend heavily on current and future air pollution legislation. Air quality standards and the federal and state regulations enacted to achieve those standards may directly or indirectly dictate the use of specific NO_x control technologies. Therefore, the purpose of this chapter is to review those NO_x regulations currently in effect and to examine the prevalent trends in NO_x legislation. Since NO_x is a participating species in reactions leading to the formation of photochemical oxidants, references will also be made to oxidant legislation.

4.1 Current NO_x Regulations

The enactment of the Clean Air Act in 1963 provided the foundation for a series of other federal and state government actions designed to limit atmospheric emissions of specific compounds designated as pollutants. Since that time a number of both national and regional air quality and pollutant emission standards have been promulgated. The most notable regulations currently in effect for NO_x are the National Ambient Air Quality Standards (NAAQS), the State Implementation Plans (SIP's) regulations, the New Source Performance Standards (NSPS), and the New Mobile Source Standards. In this section, the purpose, general level of regulation, and any regional variations seen in these standards are discussed. The implications of more recent requirements (e.g., Prevention of Significant Deterioration) will be discussed in the section dealing with trends in NO_x legislation.

4.1.1 National Ambient Air Quality Standards

Although NAAQS do not regulate emissions directly, they do exert an indirect influence on emission controls. Depending upon the allowable atmospheric concentration for NO_2, regulatory guidelines within a specific region may or may not require FGT. The Clean Air Act Amendments of 1970 established two types of air quality standards, primary and secondary.

Primary standards are those set for the protection of the public health with an adequate margin of safety. For NO_2 this standard is based on health effects studies conducted in 1968-69 and in 1972. The primary ambient air quality standard for NO_2 is 100 $\mu g/m^3$ measured as an annual arithmetic mean.

Secondary ambient air quality standards are set for the protection of the public welfare. These standards address impacts upon soils, water, crops, vegetation, manmade materials, animals, wildlife, weather, visibility, climate, and personal comfort and well being. For NO_2, the secondary standard is equivalent to the primary standard, 100 $\mu g/m^3$.

According to the Clean Air Act, a state may choose to enact ambient air quality standards which are stricter than the corresponding federal standards. For NO_2, four states have done so: California, Hawaii, New Mexico, and North Dakota. These standards are summarized in Table 8.

NO_2 is considered the most toxic and potentially dangerous oxide of nitrogen found in the atmosphere. It has been studied in more detail than any of the other nitrogen oxide compounds. The existing data on health effects due to NO_2 exposure have been summarized several times. Two such summaries may be

TABLE 8. STATE AMBIENT AIR QUALITY STANDARDS WHICH ARE MORE STRINGENT THAN NAAQS FOR NO_2

State	Ambient Air Quality Standard
California	100 $\mu g/m^3$ annual arithmetic mean 470 $\mu g/m^3$ (0.25 ppm) for a 1-hour average
Hawaii	70 $\mu g/m^3$ annual arithmetic mean 150 $\mu g/m^3$ for a 24-hour average
New Mexico	100 $\mu g/m^3$ annual arithmetic mean 200 $\mu g/m^3$ for a 24-hour average
North Dakota	100 $\mu g/m^3$ annual arithmetic mean 200 $\mu g/m^3$ maximum 1-hour concentration

Source: Reference 28.

found in References 29 and 30. Criteria documents for the short-term and annual average standard for NO_2 are in preparation and will include summaries of health effects data also. The graphical summaries presented in Figures 1 and 2 show the levels of NO_2 at which health effects have been observed and their relation to the level dictated by the National Ambient Air Quality Standards for NO_2. Most of the effects reported have been on the respiratory system, but some NO_2 health system effects have also been reported. The lowest reported level of NO_2 which has been associated with human health effects is 200 $\mu g/m^3$ (0.1 ppm). This level reportedly caused bronchioconstriction in 13 out of 20 asthamatics tested (Reference 31). The work is highly controversial, however, and will have to be confirmed by further studies.

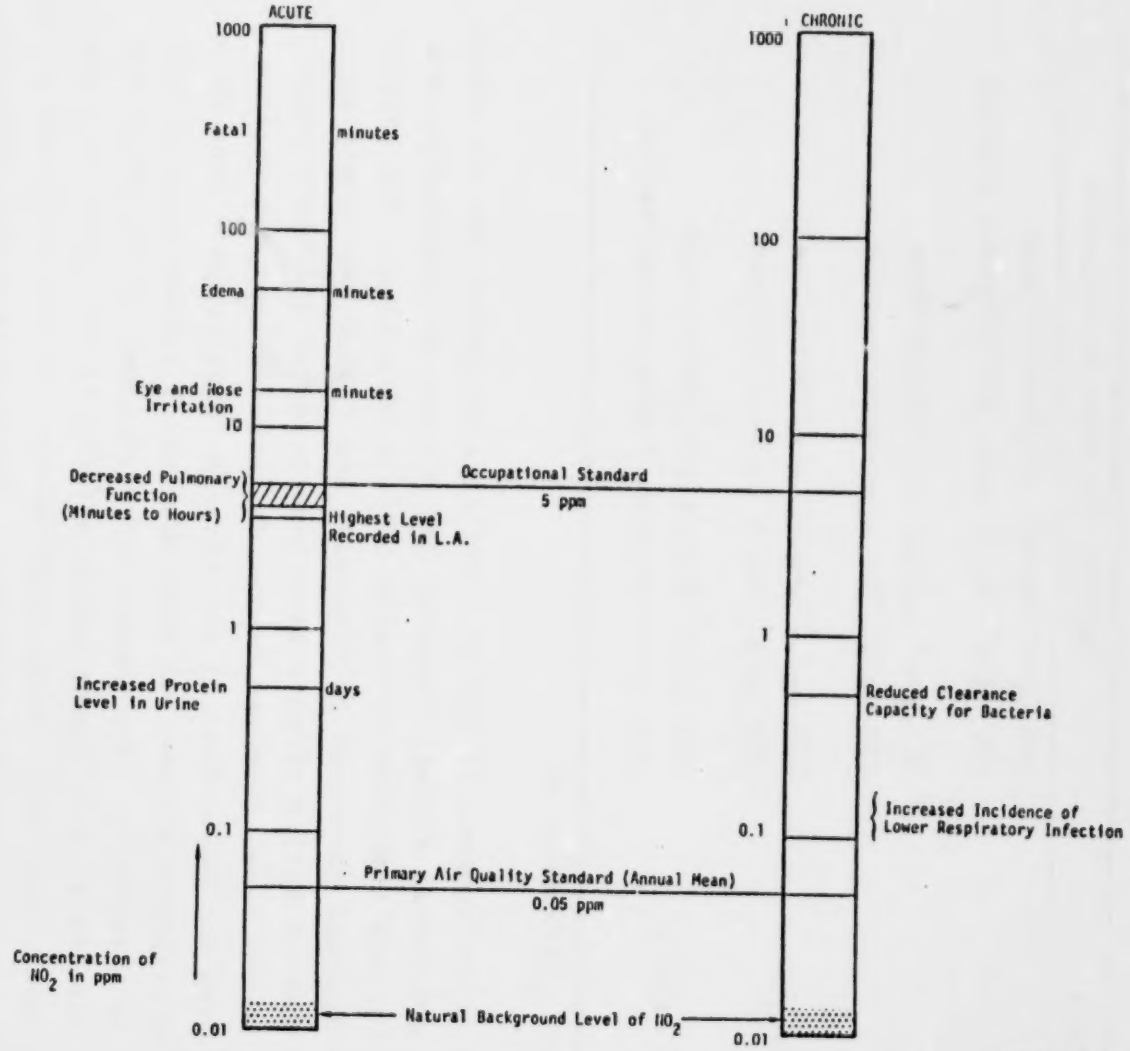

Figure 1. Observed Effects of NO_2 on Humans.

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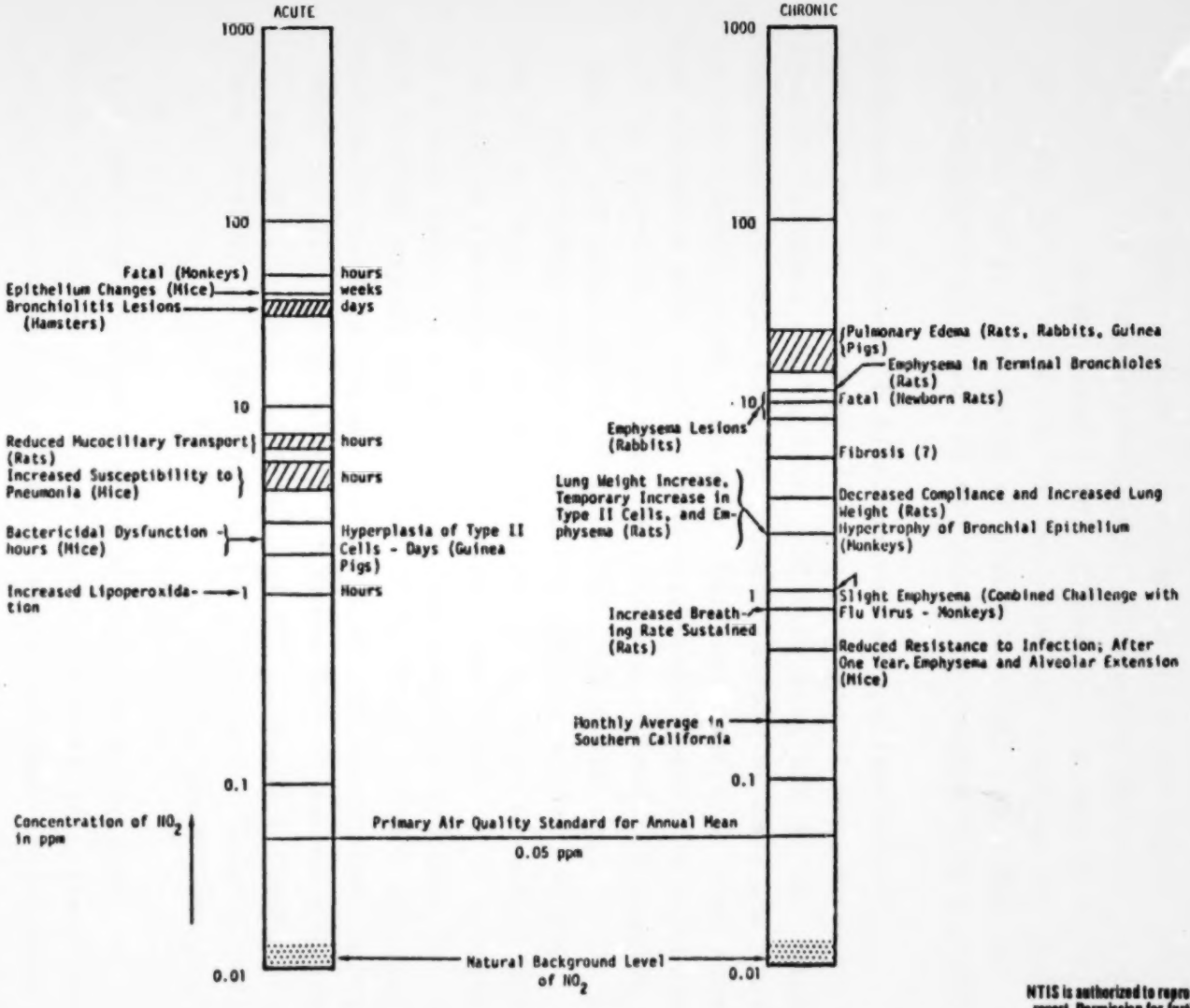

Figure 2. Observed Effects of NO_2 on Animals.
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Although the present state of knowledge indicates that NO_x acts as a precursor in the formation of photochemical oxidants, as of yet, there has been no attempt to control ambient oxidant levels by limiting ambient NO_2 levels (Reference 32). For the protection of the public health, the Primary Ambient Air Quality Standard for oxidants has been set at 160 $\mu g/m^3$ (0.08 ppm) for a one-hour exposure. This standard is based on a series of health studies, a good summary of which can be found in Reference 33.

Additionally, the new criteria document for photochemical oxidants, now in preparation, will contain a health effects summary. As is the case with NO_2, most of the reported oxidant effects are seen in the respiratory system. Some extrapulmonary effects have also been reported, however. Dose response curves constructed by recent human exposure studies show pulmonary system effects for healthy subjects exposed to O_3 at levels of 720 $\mu g/m^3$ (0.37 ppm) and higher for 2 hours (References 34, 35 and 36). However, there is some evidence of health effects in healthy human subjects at a level as low as 490 $\mu g/m^3$ (0.25 ppm) (Reference 37). There are indications that exposure to photochemical oxidants mixtures may cause effects at lower levels of O_3 than the 490-720 $\mu g/m^3$ (0.37 to 0.25 ppm) figure derived from O_3 alone (References 21, 38 and 39). Recent studies of exposure of healthy humans to PAN showed no physiological effects from levels commonly found in the environment. However, PAN and similar compounds are notorious eye irritants at ambient levels (References 40 and 41).

Results of related, ongoing studies of both NO_2 and oxidant health effects have the potential for effecting tighter NO_x controls if they are shown necessary to protect the public health.

State Implementation Plans

State Implementation Plans (SIPs) are the regulatory mechanisms used to achieve and maintain compliance with ambient air quality standards within a state's boundaries. The Clean Air Act requires that each state design its own control strategy to accomplish this.

Although all states are required to comply with NAAQS, each state is confronted with a different set of emission sources and resulting air pollution problems. Therefore, SIPs can vary widely from state to state. The primary objective of each SIP is to alleviate pollution problems either by controlling or eliminating specific emission sources, including both new and existing sources.

In almost every instance, only two industrial operations, combustion units and nitric acid plants, have NO_x emission limits set by SIPs. In 35 of 50 states, existing combustion units are unregulated with respect to NO_x emissions. In the remaining 15 states, the NO_x regulations for existing combustion units vary considerably. Most of these states, however, require a unit to have a heat input of at least 73 MW (250 million Btu/hr) before coming under regulation. Usually, these regulations are based on the type of fuel burned. Typical ranges for NO_x emissions limits are as follows: gas: 86-130 g/GJ (0.2-0.3 lb/10^6 Btu); oil: 130-260 g/GJ (0.3-0.6 lb/10^6 Btu); coal: 300-390 g/GJ (0.7-0.9 lb/10^6 Btu). For new, modified, or expanded combustion unit, 32 states regulate the maximum allowable NO_x emissions. For the most part, these states have adopted Federal NSPS (see Section 4.1.2) as a part of their SIPs (Reference 42).

Regulation of NO_x emissions from nitric acid plants is also somewhat varied among the states. Less than half (21) of the states have SIP regulations for existing nitric acid plants. These regulations range in the severity of their emission limits. from 1.5-20 g NO_2/kg (3.0 to 40.0 lb per ton) of acid produced. In some instances, the nitric acid plant must also meet an opacity requirement of from 5-20%. For new, modified, or expanded nitric acid plants, almost two-thirds (32) of the states have imposed SIP regulations. For the most part, these states have adopted Federal NSPS (see Section 4.1.2) and tightened the opacity requirement to less than 10% (Reference 42).

Currently there are no NO_x limitations in any SIPs aimed at the control of photochemical oxidants. Control of hydrocarbon emissions aimed at NAAQS attainment has been emphasized for oxidant control.

Unlike most states, California has an implementation plan for each county. The California NO_x regulations are usually more stringent than those found in most SIPs. For instance, in the Southern California Air Pollution District, NO_x emissions from existing steam generators are limited to 160 mg/m^3 (125 ppm) (gas) and 280 mg/m^3 (225 ppm) (liquid and solid), regardless of size. New units have even stricter NO_x limitations: 100 mg/m^3 (80 ppm) (gas), 200 mg/m^3 (160 ppm) (liquid), and 280 mg/m^3 (225 ppm) (solid) (Reference 43). Currently, a proposed regulation requiring 90% reduction from present NO_x emission levels is being considered for all utility boilers in the South Coast Air Basin.

4.1.2 New Source Performance Standards

The purpose of New Source Performance Standards (NSPS) is to prevent the degradation of existing air quality. The aim

is to avoid future air pollution problems by establishing standards of performance for new stationary sources and modified or expanded existing sources. The "standard of performance" for a new stationary source is based on the best emissions control system, which is both proven and available at a reasonable cost. The degree of emission reduction which can be achieved with this system is designated by EPA as the "standard of performance". Therefore, NSPS are a direct result of technology availability and cost.

Currently only steam generators with a heat input greater than 73 MW (250 million Btu/hr) and nitric acid plants are affected by NSPS regulations. For steam generators, NO_x emissions are regulated according to fuel: gas, 86 g/GJ (0.2 lb/10^6 Btu); oil, 130 g/GJ (0.3 lb/10^6 Btu); coal, 300 g/GJ (0.7 lb/10^6 Btu). For nitric acid plants, NSPS guidelines limit NO_x emissions to 1.5 g/kg (3.0 lb per ton) of 100% acid produced (References 44, 45 and 46).

4.1.3 New Mobile Source Standards

As is the case with New Source Performance Standards, mobile source standards are designed to prevent the degradation of existing air quality. All NO_x emission standards for motor vehicles have proven technology as their basis. The 1977 amendments to the Clean Air Act have established NO_x mobile source standards for both light- and heavy-duty gasoline-fueled vehicles or engines. For light-duty vehicles these standards set NO_x emissions limits at 1.2 g/km (2.0 g/mile) for 1977-1980 models and 0.62 g/km (1.0 g/mile) for 1981 and thereafter. For heavy-duty vehicles, the standards require a reduction of at least 75% from the average of the actually measured emissions from a vehicle or engine manufactured during the baseline model year (Reference 47).

California has adopted more stringent mobile source standards for light-duty vehicles. Currently, California limits NO_x emissions from new light-duty vehicles to 0.93 g/km (1.5 g/mile). By 1982 this NO_x limit will be further reduced to 0.24 g/km (0.4 g/mile). A waiver is granted for light-duty vehicles using diesel engines. Diesel light-duty vehicles are limited to 0.93 g/km (1.5 g/mile) for the years 1981-1984.

4.2 Trends in NO_x Legislation

Future trends in NO_x legislation will continue to be driven by the results of health effects research and advances in emission control technologies. In addition, the link between ambient NO_x and the production of photochemical oxidants may lead to NO_x legislation aimed at oxidant control. This will depend on the research findings concerning the mechanism of photochemical oxidation. At present, no NO_x regulations are specifically designed for that purpose. The possibility that several AQCRs are approaching noncompliance status with respect to ambient NO_2 levels may also provide incentives for future, more stringent NO_x legislation.

The Clean Air Act Amendments of 1977 will have a significant impact on future NO_x regulations in that they require each state to submit a revised SIP that provides for the attainment of primary NAAQS for NO_2 by December 31, 1982. The new SIP must also provide for the attainment of NAAQS for areas experiencing severe oxidant problems by December 31, 1987. Revised SIPs will also have to address two new source regulatory policies: emissions offset and prevention of significant deterioration (PSD).

The offset policy requires that a permit program be established for new or modified major facilities. Under this

program, emissions from new sources must be either within new growth allowances built into the revised SIP or be offset by a reduction in emissions from another source within the area. Cost will be a determining factor, but will be given less emphasis than in the case of NSPS.

The PSD policy provides for the protection of public health and welfare and the preservation, protection, and enhancement of all Class I areas (national parks, monuments, forests, preserves, and recreation areas). Significant deterioration is measured by pollutant levels and visibility. New stationary sources seeking to locate in Class I areas must meet preconstruction requirements ensuring that NO_x emissions from the source will not exceed an allowable increment for NO_x. New sources are also required to use the best available control technology. The visibility stipulations include color as well as visibility reduction. Nitrogen dioxide contributes to both conditions since it is both a precursor to photochemical smog and a brown gas.

Preconstruction requirements must also be met for new or modified sources in non-attainment areas. In these cases, the source must comply with the Lowest Achievable Emission Rate (LAER) before being permitted for construction and operation.

Based on data which indicate that short-term exposures to NO_2 may cause adverse health effects, the 1977 CAA amendments may require EPA to set a short-term NO_2 ambient air quality standard. Discussions with EPA's Office of Air Quality Planning and Standards indicate that this standard will probably range from 200-1000 $\mu g/m^3$ for a one to three hour average.

As technological advances are made, regulations reflecting the state-of-the-art of control technology will change. These

regulations include New Source Performance Standards and New Mobile Source Standards. Currently, NSPS regulations for NO_x from electric utility generating stations are being considered for revision. The new standards proposed on September 19, 1978 apply to electric utility steam generating units capable of firing more than 73 MW (250×10^5 Btu/hr) heat input of fossil fuel. A summary of the provisions applicable to the most common fuels are summarized in Table 9.

TABLE 9. SUMMARY OF NSPS FOR NO_x EMISSIONS FROM ELECTRIC UTILITY GENERATING STATIONS

Fuel	Proposed NSPS
natural gas	86 g/GJ (0.2 lb/10^6 Btu)
oil	130 g/GJ (0.3 lb/10^6 Btu)
coal	260 g/GJ (0.6 lb/10^6 Btu)
lignite	210 g/GJ (0.5 lb/10^6 Btu)

Source: Reference 48.

Several new emission source categories are also being investigated. Screening studies are underway for adipic acid manufacturing, dimethylterephthalate/terephthalic acid plants, explosives (high and low), fiberglass, textile, and wool manufacturing, to determine the need for NO_x NSPS. Technical studies are either in progress or completed for stationary internal combustion engines (diesel and gasoline), stationary gas turbines, and steam generators with a heat input of 0.09-73 MW (0.3-250 x 10^6 Btu/hr) (gas, oil, and coal) to provide detailed information for NO_x NSPS (References 44 and 45).

Mobile source standards may change somewhat. Currently, the 1982 California standard of 0.24 g/km (0.4 grams per

mile) appears to represent the best level achievable with available control technology.

In summary, it appears that current trends in NO_x regulations are toward more stringent control of all sources.

5.0 CONTROL STRATEGIES

Unless a level of control requiring FGT is adopted by some future NSPS, the question of "if and when" FGT will be necessary will ultimately be decided in the development of NO_x control strategies such as the ones included in State Implementation Plans. Strategies for control of NO_x cannot be developed on a national level because the NO_x problem is a very area-specific one which depends on topography, meteorology, and emission source characteristics.

The purpose of this section is not to develop control strategies for individual AQCR's but to determine how strategies for attaining and maintaining compliance with various sets of standards affect the need for FGT technology. The various technologies for controlling NO_x emissions from stationary sources and mobile sources are considered. The manner in which these control techniques might be applied to attain or maintain compliance with various standards is discussed.

5.1 Methods of Control

Techniques that will reduce NO_x emissions from both stationary and mobile source fossil fuel combustion fall into two general categories: combustion modification (CM) which limits NO_x formation and post-combustion flue gas treatment (FGT). A variety of techniques and processes are available or under development in each of these areas. In the following subsections the status of development, cost effectiveness and technical limitations of both of the generic classes of processes are briefly discussed. Further information on specific techniques and processes is given in Appendix A.

5.1.1 Stationary Sources

Major sources of concern in the development of an NO_x control strategy for stationary sources are utility boilers and large industrial boilers and furnaces. In 1975, contributions from this class of sources to total NO_x emissions in each of the twenty problem AQCR's previously discussed ranged from 10-80%. In five of the AQCR's, utility boilers alone accounted for 40% or more of the total NO_x emissions.

The control techniques that have been developed or are currently undergoing development for those sources are: combustion modification, fluidized bed combustion, and flue gas treatment. Other stationary sources which have been indicated as major contributors to NO_x emissions in some areas are commercial and residential furnaces (Reference 49). Since control techniques for these small sources are being studied and/or developed at this time, definitive cost data are unavailable. Comparative costs for CM and FGT as applied to large combustion sources are shown in Table 10. The economics of fluidized bed combustion are not yet well established, and therefore, the cost effectiveness of this approach to NO_x control cannot be assessed at this time.

TABLE 10. COMPARATIVE COSTS OF STATIONARY SOURCE CONTROLS

Source	Type of Control	Level of Control	Cost
Utility Boilers	Combustion modification:		
	New Boilers	30-50%	\$110/Mg NO_x (\$100/ton NO_x)
	Retrofit	30-50%	\$248/Mg NO_x (\$225/ton NO_x)
	Flue Gas Treatment		
	Selective catalytic reduction	50-90%	\$1320/Mg NO_x (\$1200/ton NO_x)
	Fluidized Bed Combustion	40-70%	-
Industrial Boilers	Combustion Modification	25-65%	\$165/Mg NO_x (\$150/ton NO_x)

Source: Reference 50.

As indicated in Table 10, in most stationary source applications, combustion modifications will be the most cost effective technique for reducing NO_x emissions. There are several combustion modification techniques available for control of stationary sources. These include low excess air (LEA) firing, staged combustion, flue gas recirculation (FGR), burner modification and steam injection. All of these techniques reduce the formation of NO_x in a boiler or furnace by either lowering the flame temperature or lowering the oxygen concentration in the flame front, or both. The best technique or combination or techniques will be a function of the degree of removal required and the effect of the modification on process economics. Currently, the most significant potential disadvantage of combustion modification is that some techniques create a reducing atmosphere in the lower section of the boiler which may lead to accelerated tube wastage. Tests are currently underway to resolve the issue of tube wastage during substoichiometric firing. If these tests indicate no significant wastage, then new boilers can be expected to be equipped with provisions for LEA and staged combustion. The additional need for and value of FGR has not yet been definitely established. Combustion modifications will generally be the first retrofit technique applied to existing boilers in areas where ambient air quality standards are being exceeded. This is already the case in California (Reference 51).

Fluidized bed combustion (FBC) is an emerging technology specifically applicable to coal. The feature of FBC which affects NO_x emissions is the relatively homogeneous temperature of about 840°C (1550°F) which exists throughout the bed. Conventional boilers have a temperature gradient from the flame to the wall with flame temperatures on the order of 1370°C (2500°F). The lower combustion temperature of FBC kinetically inhibits formation of thermal NO_x and, thereby, leads to lower NO_x emissions. FBC is currently being tested on a large scale (30 MWe) test

unit and is expected to be available commercially within the next decade (Reference 52). However, the extent to which FBC will be applied cannot be determined at this time. Currently, the impetus for development of FBC is not its NO_x reduction capability, but rather its combination of advantages over a conventional boiler followed by a flue gas desulfurization (FGD) unit.

Flue gas treatment differs from combustion modification and fluidized bed combustion in that NO_x is reduced or removed from the flue gas after formation. Generally, FGT processes will be significantly more expensive than combustion modification. As a result, it is likely that FGT processes will be applied only in addition to combustion modification in situations where additional control is necessary.

The NO_x-only FGT processes, both catalytic and noncatalytic selective reduction, will soon be in a stage of development which will allow commercial application. In fact, demonstration of this technology has been ordered by CARB.

Current economics seem to indicate that the most promising combination for maximum NO_x and SO_2 control from a conventional coal-fired boiler appears to be application of 1) LEA and staged combustion, 2) a selective catalytic or noncatalytic FGT system, and 3) a conventional FGD unit. However, in every application, there will be specific technical and economic factors which will determine the best combination of control options. As further development of simultaneous NO_x/SO_2 FGD processes continues, it may be demonstrated that it is more economical to operate a single simultaneous NO_x/SO_2 removal process than two individual processes in situations where removal of both pollutants is required (see discussion in Appendix A).

5.1.2 Mobile Sources

The major mobile sources of concern in the development of an NO_x control strategy are light duty vehicles (passenger cars), light duty trucks (pick-ups and vans), and heavy duty vehicles (trucks and buses). In 1975, contributions from this class of sources to total NO_x emissions in each of the twenty problem AQCR's previously discussed ranged from 15-61%. In eight of those AQCR's mobile source emissions accounted for more than 50% of the total NO_x emissions. The NO_x control techniques that have been developed or are currently undergoing development for these sources are combustion modification and catalytic reduction. Comparative costs of mobile source emission controls as a function of source type and level of control achievable are shown on Table 11.

TABLE 11. COMPARATIVE COSTS OF MOBILE SOURCE CONTROLS

Source	Type of Control	NO_x emission reduction From	To	Cost
Light duty vehicles and Light duty trucks	Combustion Modification	1.2 g/km (2.0 g/mile)	0.62 g/km (1.0 g/mile)	\$500/Mg NO_x (\$450/ton NO_x)
Light duty vehicles	Catalytic Reduction	0.62 g/km (1.0 g/mile)	0.24 g/km (0.4 g/mile)	\$2530/Mg NO_x (\$2300/ton NO_x)
Heavy duty diesel	Combustion Modification	12.6 g/km (20.3 g/mile)	3.7 g/km (6 g/mile)	\$450/Mg NO_x (\$410/ton NO_x)
Heavy duty gasoline	Combustion Modification	8.6 g/km 13.8 g/mile	1.9 g/km (3 g/mile)	\$740/Mg NO_x (\$669/ton NO_x)

Source: Reference 50.

Combustion modification for NO_x control has been applied to light and heavy duty vehicles for several years. The techniques employed (air/fuel ratio control, exhaust gas recycle, stratified charge, etc.) are very similar, both in concept and in practice, to the combustion modification techniques previously discussed for stationary sources. However, the cost of combustion modifications is roughly three to four times higher for mobile sources per ton of NO_x removed than for stationary sources.

Exhaust gas treatment (use of catalytic converters) has not yet been commercially applied to light duty vehicles. (Catalytic converters for NO_x control should not be confused with those currently in use for hydrocarbon control). The costs for this post combustion cleanup are estimated to be approximately twice the estimated costs for stationary source FGT on a per ton of NO_x removal basis. Considerable research and development is underway to develop this technology in anticipation of tighter federal standards. Regardless of the final decision on Federal mobile source standards, exhaust gas treatment will be required in some states (notably California) in order to meet state standards.

In addition to the high costs associated with post-combustion NO_x control of mobile sources, there are other mobile source control problems to be considered. The number of sources to be controlled is huge relative to the number of large stationary sources, making retrofit to existing sources virtually impossible. In addition, consideration must be given to guaranteeing proper maintenance and inspection of controls.

5.2 Attainment and Maintenance of Standards

The NO_x standards which impact the need for FGT can be classified into two groups: emission standards and ambient

air quality standards. The emission standards of interest are Federal NSPS and any state regulations adopted in SIPs.

The ambient air quality standards of interest are the Annual Average NO_2 NAAQS, the recently mandated Short Term NO_2 NAAQS individual State, short term NO_2 standards, and PSD requirements. The degree to which attainment and maintenance of each of these standards affects the need for FGT is discussed in the following subsections.

5.2.1 New Source Performance Standards

NO_x emissions vary with the type of fuel used and the method of firing the fuel. Typical uncontrolled emissions for various fuels are shown in Table 12. Also shown are the emission limits specified by current NSPS and the percent NO_x reduction corresponding to those limits.

TABLE 12. TYPICAL UNCONTROLLED NO_x EMISSIONS FROM LARGE FOSSIL FUEL-FIRED STEAM GENERATORS

Fuel	NO_x Emissions g/GJ (lb/10^6 Btu)	NSPS g/GJ (lb/10^6 Btu)	% Reduction Required to meet NSPS
Natural Gas (1050 Btu/ft^3)	27 - 200 (0.062 - 0.47)	86 (0.2)	0-57
Fuel Oil (150,000 Btu/gal)	37 - 350 (0.13 - 0.81)	130 (0.3)	0-63
Coal (11,900 Btu/lb)	149 - 470 (0.32 - 1.1)	300 (0.7)	0-36

Source: Reference 53.

Congress in the 1977 Clean Air Act Amendments mandated that the current NSPS be reviewed and revised as appropriate. FGT is not being required by the revised Federal NSPS for large steam generators. Although the NSPS are being tightened, they specify a level of emissions attainable through use of combustion modification techniques alone. This means that for the near term, new and expanding sources will not be required to use FGT to comply with the Federal NSPS. However, it should be noted that FGT technology is being evaluated to determine its feasibility as the basis for a NSPS for steam generators with less than 73 MW (250 Btu/hr) heat input.

Table 13 shows the IERL/RTP research goals for stationary source NO_x emission reduction. It is quite likely that as these goals are achieved, the NSPS will again be reviewed.

If the technical and economic feasibility of applying new control technology can be demonstrated, it is very possible that the NSPS will be reviwed to require emission limits substantially lower than those currently established or proposed. The 1985 goal for coal-fired utility boilers of 125 mg/m^3 (100 ppm) NO_x emitted at 3% O_2 is roughly equivalent to 64 g/GJ (0.15 $lbs/10^6$ Btu). This level of control would either require FGT or a substantial improvement in the current state-of-the-art of combustion modification.

5.2.2 Annual Average Ambient Air Quality Standard

Currently the only oxide of nitrogen for which air quality standards exist is nitrogen dioxide (NO_2). In Section 3.0 it was shown that NO_x emissions from direct fossil fuel combustion account for more than 90% of the total U.S. anthropogenic emissions of NO_x. As a result, any strategy for controlling the ambient concentration of NO_2 or secondary NO_x pollutants

TABLE 13. EPA R&D PROGRAM NO_x CONTROL TARGETS

Source	mg/m^3 NO_x (ppm NO_x) at 3% Excess O_2		
	Current Technology	1980 Goal	1985 Goal
Utility boilers			
Gas	188 (150)[a]	125 (100)	62 (50)
Oil	280 (225)[a]	188 (150)	112 (90)
Coal	688 (550)[a]	250 (200)[c]	125 (100)
Industrial boilers			
Gas	188 (150)	100 (80)	62 (50)
Residual oil	406 (325)	156 (125)	112 (90)
Coal	560 (450)	188 (150)[c]	125 (100)
Reciprocating engines			
Spark ignition-gas	3750 (3,000)	1500 (1,200)[d]	500 (400)
Compression ignition-oil	3125 (2,500)	1500 (1,200)[d]	1000 (800)
Gas turbines			
Gas	500 (400)[b] 188 (150)[b]	94 (75)[d]	31 (25)
Oil	750 (600)[b] 280 (225)[b]	156 (125)[d]	31 (25)

[a]Current NSPS.

[b]Estimated achievable with wet control technology.

[c]Developed and field-applied technology.

[d]Developed technology.

Source: Reference 54.

must concentrate or reducing NO_x emissions from fossil fuel combustion.

As shown in Section 3.0, there are only a few AQCR's currently out of compliance with the National Ambient Air Quality Standard for NO_2 of 100 $\mu g/m^3$ measured as an annual arithmetic mean. Furthermore, the margin by which the air quality standard is exceeded is small. Because of these facts, stringent NO_x emission controls such as FGT have to date not been required in order for AQCR's to attain compliance. There has been concern expressed, however, that growth will cause many more AQCR's to be out of compliance with the annual average standard and by a wider margin than those seen today (Reference 55). If the NO_2 problem worsens, there may be more impetus for implementing more stringent control measures such as FGT.

Twenty AQCR's which potentially have a problem attaining or maintaining compliance with NO_2 ambient air quality standards were identified in Section 3.0. The emissions profiles in 1975 for these twenty problem AQCR's are presented in Table 4. It is obvious from an analysis of this data that identical control strategies would not be appropriate for all twenty AQCR's. Some of the AQCR's are dominated by stationary sources, some by mobile sources. Strategies for controlling ambient concentrations of NO_2 and secondary NO_x pollutants in any given AQCR should, therefore, be developed on a case by case basis considering not only the emissions inventory for the specific AQCR under consideration, but also such diverse factors as the topography and meteorology of the area.

If the decision is made that NO_x emissions must be reduced to attain or maintain the annual average air quality standards in a given AQCR there are several options to be considered in development of a viable control strategy.

Tightening mobile source emission standards is one control option for AQCR's experiencing difficulty in meeting the annual average standard. The Federal mobile source emission standard has recently been lowered. Emissions for 1977-1980 models are limited to 1.2 g/km (2.0 g NO_x/mile), and for the 1981 and later models they are limited to 0.62 g/km (1.0 g NO_x/mile). Control strategies for problem areas that are mobile source dominated might include lowering the standards even more until the practical limit of 0.4 g NO_x/mile is reached. As was shown in Section 5.1.2 the cost of this control option is very high and many technical and administrative problems have to be considered.

Another option for AQCR's experiencing difficulty in attaining or maintaining the annual average NO_2 standard, especially one in which the NO_x emissions are stationary source dominated, would be to tighten stationary source emission regulations. As was discussed in Section 5.1.1, if it is considered necessary to tighten controls on NO_x emissions from large stationary sources, CM techniques are the usual first step because of the high cost (per ton NO_x removed) of FGT. However, application of FGT could be considered if the practical limit of control by combustion modification had been reached and additional reductions in NO_x emissions were required for attainment or maintenance of the standard.

In light of the uncertainties discussed in Section 3.0, with respect to the exact relationship between emissions of NO_x and ambient concentrations of NO_2, it is highly probable that the most common control strategy that would be applied to a problem AQCR would represent a combination of the two options discussed above. Using the comparative costs previously presented as a guide to cost effectiveness, the first controls to be applied would be combustion modification of stationary sources. This

would be followed by combustion modification of mobile sources. If additional reductions were required, FGT would be applied to stationary sources and finally to mobile sources.

5.2.3 Short-Term Standard

Congress has directed EPA to set a short-term standard for NO_2 unless it is deemed unnecessary for the protection of public health. It is not clear how many AQCR's would have trouble complying with this type of standard, but it is generally assumed that a short-term standard would be a stricter standard than the current annual average standard. A number of AQCR's that have potential problems complying with the annual average standard can be expected to also have problems complying with the short-term standard.

The control options for attaining and maintaining compliance with a short-term standard would be the same as those discussed in the previous section on the annual average standard. However, it should be noted that FGT might be required in some AQCR's to meet a short-term standard, even though it might not have been required to meet the annual average standard.

Other areas of uncertainty exist in the comparative contributions of stationary and mobile sources to the high short-term levels. It is possible that both types of sources could contribute to peak concentrations. Conditions under which plumes might impact ground level with very little dispersion are presented in Section 3.3. However, rush hour traffic has been demonstrated as a cause of high NO_2 levels from mobile sources in many cities and mobile sources are thought to be major offenders, as illustrated in Figure 3 for Southern California. Strategies for lowering peak NO_2 levels have not yet been developed. Attempts may be made to lower peaks by reducing back-

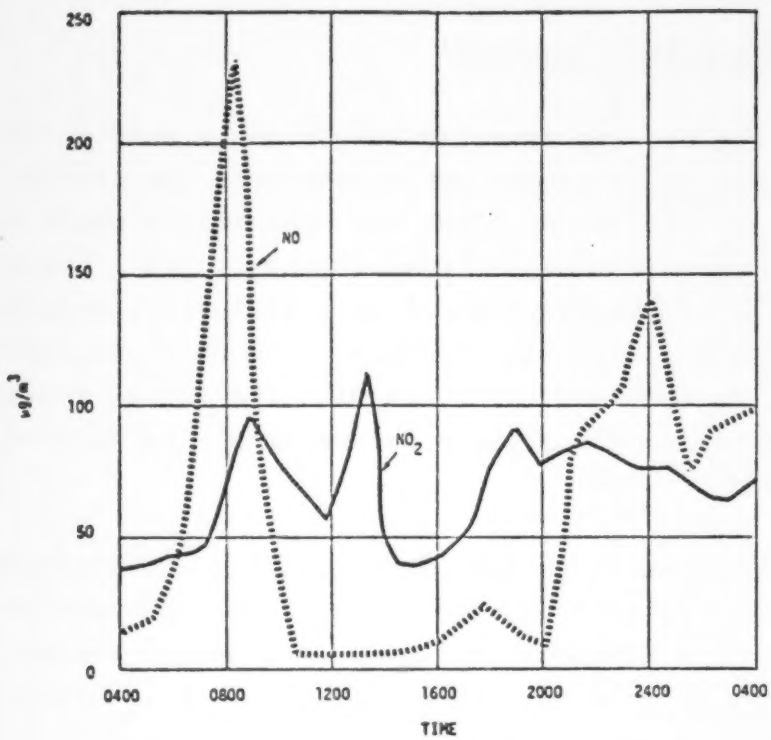

Figure 3. Variations in NO and NO_2 in Orange County, California, October, 1974.

Source: Reference 29.

ground levels. If this is the case, stationary source controls such as FGT may be indicated.

Several states have existing short-term standards. California is a noteable example because of the stringency of the standard and because of the severity of the NO_2 problem in the South Coast Air Basin (SCAB). The California standard is 500 $\mu g/m^3$, one hour maximum. In an effort to achieve the standard, mobile source emission standards are being lowered to 0.24 g/km (0.4 g/mile). Combustion modification techniques have already been implemented in the SCAB. The California Air Resources Board (CARB) believes that in addition to these controls, FGT systems will be required for large combustion sources.

The NO_x problem is a severe one in California. CARB estimates that even if all stationary source emissions were eliminated and the 0.24 g/km (0.4 g/mile) mobile standard were implemented, compliance with the 500 $\mu g/m^3$, one-hour NO_2 standard would only be marginally achievable in the South Coast Air Basin.

In a related study (Reference 56) calculations for the Chicago AQCR have indicated that FGT may be required to attain and maintain compliance with a short-term NO_2 standard, depending on the level and averaging time selected for the standard. With a one-hour standard of 500 $\mu g/m^3$ some FGT would be required. If the standard were 250 $\mu g/m^3$ (one-hour maximum), considerable FGT would be required. However, for Chicago, the study showed that compliance with a one-hour standard of 750 $\mu g/m^3$ could be attained by use of combustion modification alone.

Whether other areas in the U.S. will have similar problems complying with a short-term standard remains to be seen.

The range of concentrations currently under consideration by EPA for the one-hour maximum is 200-1000 $\mu g/m^3$. Obviously the impact of the proposed short-term NO_2 standard cannot be fully assessed until there is final resolution of the level and the averaging time allowed.

5.2.4 Prevention of Significant Deterioration

The previous discussion has centered on devising control strategies for bringing air quality in noncompliance or near noncompliance areas within an acceptable range. There is another factor to consider in control strategy development for all AQCR's. The Clean Air Act Amendments of 1977 have specified that control strategies for prevention of significant deterioration (PSD) of air quality must be developed. NO_2 is specifically mentioned with allowable increments of increased NO_2 concentrations to be set in the near future. It is conceivable that under these provisions new fossil fuel-fired power plants and other large fossil fuel burning stationary sources might have to employ stringent NO_x emissions controls to be allowed to locate in certain areas. As previously discussed, if the emission controls needed for stationary sources require more than 50% NO_x emissions reductions, application of FGT would be indicated. Wilderness and national park areas have been given special emphasis with respect to nondegradation provisions. Protection of air quality in these Class I areas is considered of primary importance. Because of this, PSD may require FGT on any stationary fossil fuel burning source located in such an area in order to protect the pristine quality of the air even where NSPS and NAAQS would not indicate the need for FGT.

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APPENDIX A

STATIONARY SOURCE NO_x CONTROL TECHNOLOGY DESCRIPTIONS

COMBUSTION MODIFICATION

In order to understand how combustion modifications reduce NO_x it is useful to examine some of the chemistry of NO_x formation. Only a brief description is given here. To begin with, there are two mechanisms of NO_x formation. In one mechanism, NO is formed by reaction of oxygen with chemically bound nitrogen in the fuel. The amount of NO formed in this manner is roughly a function of fuel nitrogen and excess air concentrations with higher levels increasing NO formation. In the other mechanism, NO is formed through reaction of oxygen with nitrogen in the combustion air. This reaction is governed primarily by the flame temperature with increased NO formation occurring at higher temperatures. NO formed by these two mechanisms is called "fuel NO_x" and "thermal NO_x," respectively. The contribution of each reaction to the total amount of NO formed varies with fuel type and boiler configuration.

Combustion modification techniques that reduce these emissions do so by altering one or both of the primary NO_x formation mechanisms. This means either reducing the oxygen concentration, lowering the flame temperature or both. In the sections that follow, each of the currently viable techniques is examined with respect to:

- principle of operation,
- status of development,
- operating experience,
- advantages/disadvantages, and
- costs.

Both new and retrofit situations are considered.

Low Excess Air

Operating at low excess air (LEA) involves providing combustion air at an air/fuel ratio close to the theoretical air requirement for stoichiometric combustion. Without LEA firing, boilers are operated with ~30% excess air to assure complete fuel combustion. Higher excess air levels are not efficient since they lead to excessive heat loss in the flue gas. The level to which excess air can be reduced and still maintain complete combustion is a variable that must be determined empirically for each specific application. For example, less excess air is required when LEA is used singly than when it is used in conjunction with other combustion modification techniques. LEA firing is achieved by closing down on the combustion air dampers until the desired flue gas O_2 concentration is attained. When used in conjunction with staged combustion, a portion of the excess air is supplied by overfire air nozzles. In this situation, the overfire air dampers serve to regulate the amount of excess air.

LEA firing, while practiced since the 1950's, was not applied to any great extent, until recently, due to the disadvantages associated with this mode of operation. Running the boiler at minimum excess air levels has the advantages of some increase in boiler efficiency and decreased corrosion. On the other hand there are the disadvantageous effects of increased hydrocarbon and carbon monoxide emissions, increased ash generation with oil fuels and decreased carbon conversions with coal fuels.

LEA has been applied recently on many utility boilers since it is one of the most economical means of achieving a reduction in NO_x emissions. LEA firing is usually applied in conjunction with staged combustion because this modification offsets

the disadvantages of LEA firing. With LEA alone, NO_x removals on the order of 30% have been experienced with all fuel types (Ref. A-1).

The cost of installing LEA on various boiler sizes is shown in Figure 1. The plot shows that there are economies of scale in which costs are lower for larger units. It also shows similar costs for gas and oil-fired boilers (about $1/kW). LEA costs for coal-fired units are higher (about $1.25/kW).

Staged Combustion

The creation of a reducing atmosphere by staged combustion involves a first stage of combustion in which the fuel is incompletely burned by a substoichiometric amount of air. The combustion is completed above the burners where air is supplied through overfire air ports. Conversion of fuel bound nitrogen to NO_x is reduced via the reducing atmosphere in the substoichiometric stage. In the reducing atmosphere, the fuel bound nitrogen tends to form N_2 rather than NO. In addition, the flame temperature is lower in the fuel-rich zone which reduces formation of thermal NO.

Staged combustion cannot be retrofitted to all existing boilers. Application to new boilers involves installation of overfire air ports above the combustion zone, however, this is often not possible with existing boilers due to structural constraints. In retrofit situations there are several ways to approach staged combustion. One approach is to take burners out of service and use them purely as air injection ports with the remaining burners operating substoichiometrically. Alternatively, some of the burners can be operated fuel-rich and the remainder fuel-lean. A typical staged combustion configuration is shown in Figure 2.

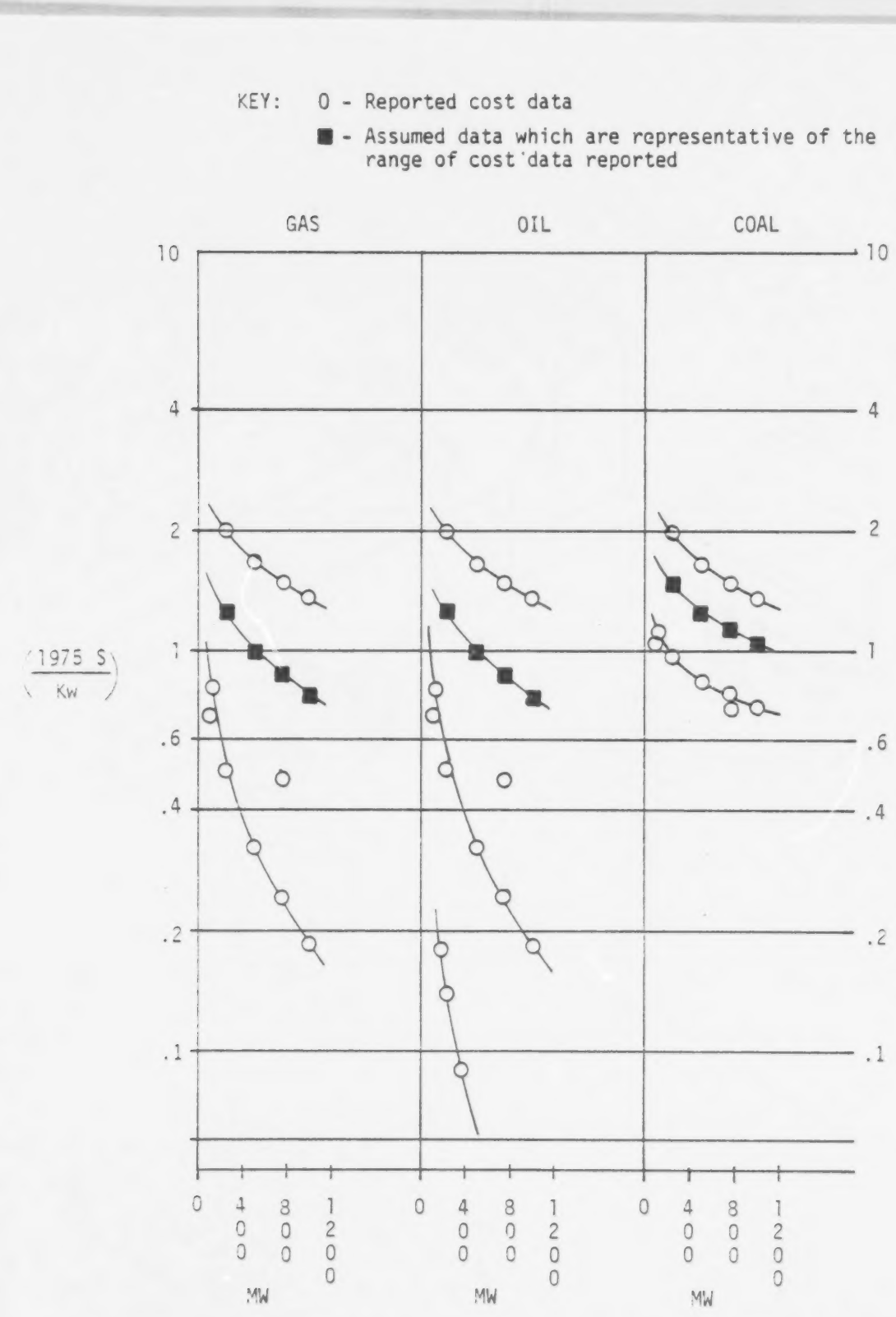


Figure 1. Cost of low excess air firing.
(Source: Reference A-1)

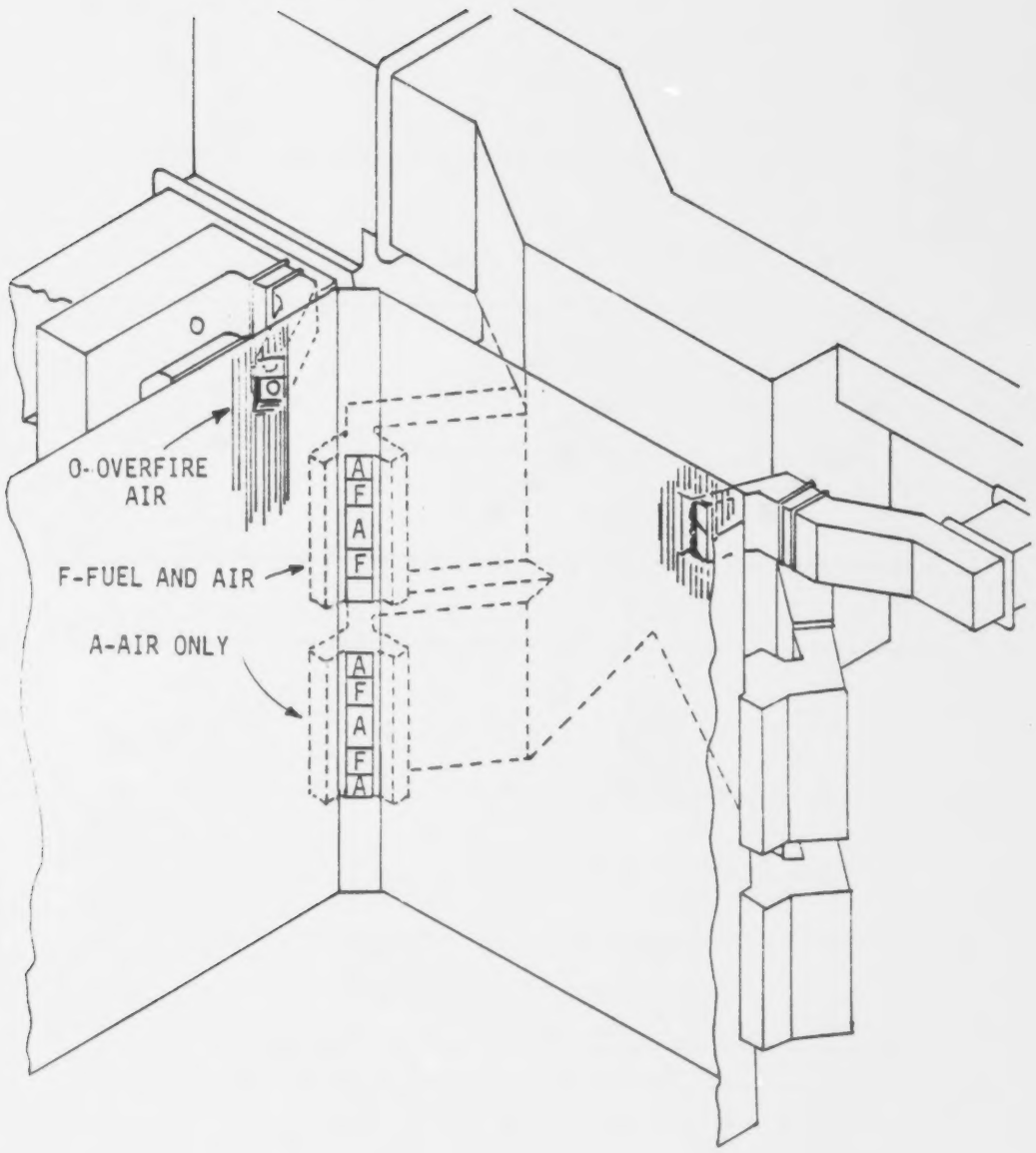


Figure 2. An example of a staged combustion configuration. (Source: Reference A-2)

Like LEA, staged combustion for NO_x control was developed in the 1950's, but has not seen widespread use until recent years. It is becoming a popular control technique when used in conjunction with LEA firing, since these two modifications have offsetting effects on boiler operation. There are some potential problems when modifying an existing boiler, however. If the total fuel flow cannot be delivered with the air injection nozzles taken out of fuel service, then boiler capacity may be limited. Staged combustion will, most likely, be retrofitted only to large boilers which have many burners, flexible fuel flow and adjustable secondary air registers. Emission reductions with staged combustion alone range from 50% with gas to 30% with coal (Ref. A-1).

Advantages of staged combustion are that it requires only minor equipment modifications and that the cost is low if boiler capacity is not affected. Disadvantages are that it cannot be applied to all boilers, it can affect flame characteristics, and it creates a reducing atmosphere in the substoichiometric combustion zone. This corrosive reducing atmosphere occurs even when staged combustion is used in conjunction with LEA and is currently a topic of industrial concern, particularly with respect to tube wastage (tube wastage rates are potentially higher in a reducing atmosphere). Tests to determine these rates have so far been inconclusive with some investigators finding increased wastage (Ref. A-3) and others finding no effect (Ref. A-2). The results of some long-term (one year) tests (Ref. A-2) should be available in the near future to help resolve this question.

Costs for implementing staged combustion are shown in Figure 3. As with LEA, costs are similar for gas and oil, about $1.50/kW but higher for coal, about $2/kW.

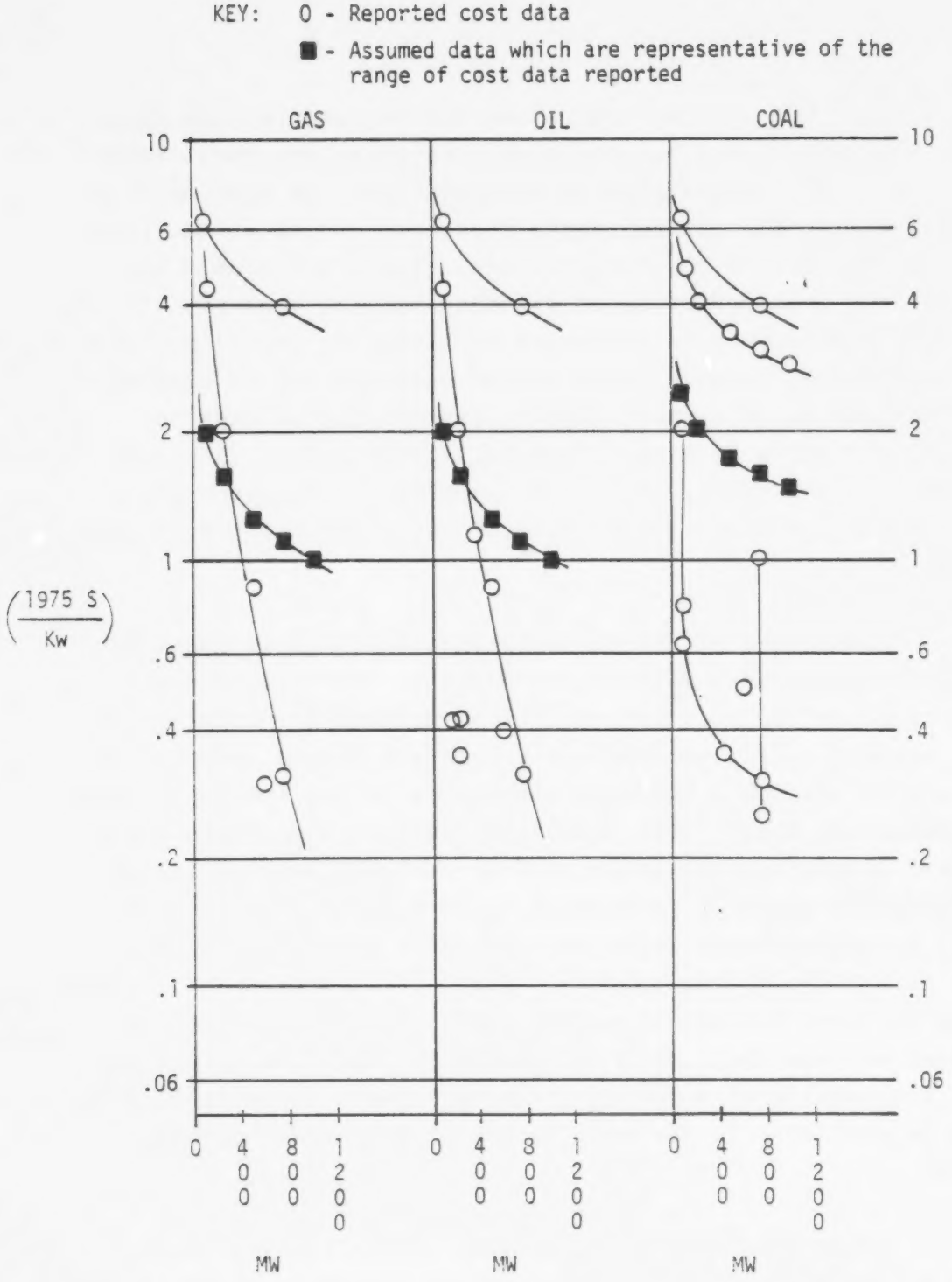


Figure 3. Cost of low excess air firing.
(Source: Reference A-1)

Flue Gas Recirculation

Flue gas recirculation (FGR), as its name implies, involves injection of flue gas into the primary combustion zone. This affects both mechanisms of NO_x formation since both the flame temperature and the O_2 concentration are reduced. FGR does require some major equipment modifications to duct work, dampers, controls and fans. FGR for temperature control has been used for the past 15-20 years, however, when used for temperature control, FGR will not reduce NO_x emissions since the flue gas is injected into the bottom of the boiler rather than into the combustion zone. FGR alone appears to be capable of achieving up to a 30% (Ref. A-1) NO_x emissions reduction with gas and oil fuels, with coal, it tends to be less effective. However, as with all combustion modifications, the actual control level achieved will vary due to conditions unique to each particular application. Potential disadvantages of FGR are increased process control complexity and vibration of recirculation ducts and fans (Ref. A-4). FGR is not being considered for NO_x control as strongly as staged combustion and LEA. This is probably due to the relative complexity of FGR with no additional benefit in NO_x reduction over other techniques.

Costs of FGR are shown in Figure 4. The equipment modifications required are reflected in the fact that FGR is more costly than the combustion modification techniques previously discussed. The costs are essentially the same for all fuels, about $3/kW.

Burner Modification

As was discussed earlier, the flame temperature can affect NO_x formation. Since different flame temperatures occur with different burner types, the firing pattern used in a given boiler is a factor in the formation of thermal NO_x. Table 1

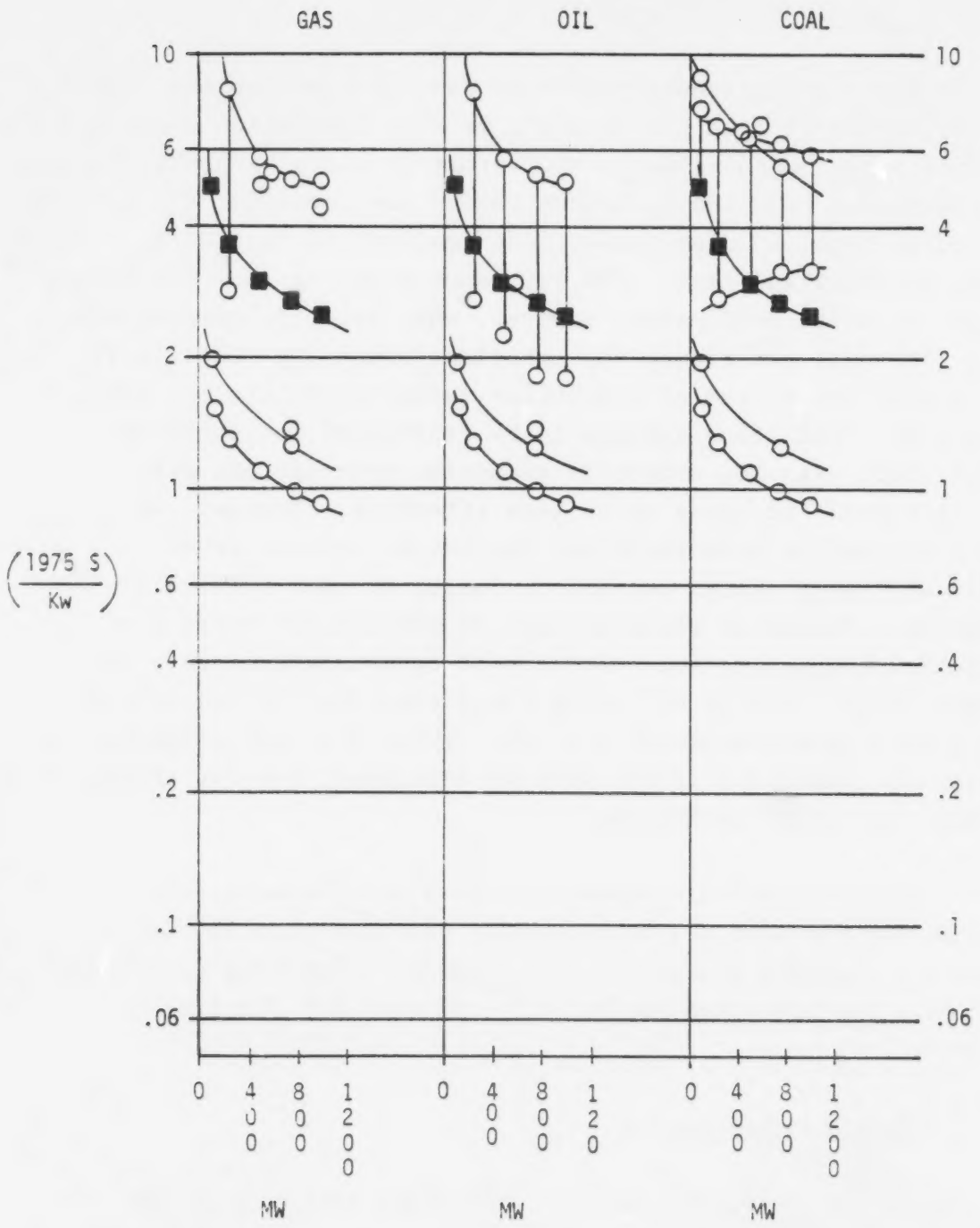


Figure 4. Cost of flue gas recirculation.
(Source: Reference A-1)

shows the effect of firing type on emissions from coal-fired power plants. Cyclone boilers generate the highest temperatures and correspondingly emit the most NO_x. Other firing methods have lower flame temperatures and NO_x emissions are correspondingly lower.

TABLE 1. TYPICAL NO_x EMISSIONS AS A FUNCTION OF METHOD OF FIRING

Method of Firing	Typical NO_x Emissions g/GJ	$lb/10^6$ Btu
Vertical	137-188	0.32-0.44
Horizontally Opposed	206-227	0.48-0.53
Spreader Stoker	244-287	0.57-0.67
Tangential (corner)	253-304	0.59-0.71
Front Wall	236-364	0.55-0.85
Cyclone	471-728	1.1 -1.7

Source: Reference A-5.

Variation of burner operating parameters have been found to have an effect on NO_x emissions. The parameters of interest include burner swirl, throat velocity and flame pattern. A number of boiler manufacturers have responded to NO_x regulations by designing new boilers to incorporate established low-NO_x burner designs (Ref. A-6). Low-NO_x burners have the advantage of adjusting to load changes more easily than other systems combustion modification techniques. No combustion modification techniques cost data were available for low-NO_x burners.

Water/Steam Injection

Water or steam can be injected into the flame zone with the effect of lowering the flame temperature. This decreases the formation of thermal NO_x. It is a very effective means of reduc-

reducing NO_x emissions; however, water injection is not widely applied due to excessive thermal efficiency losses.

Summary

Of the combustion modification techniques presented, the most promising are LEA and staged combustion. These techniques are especially attractive when used in combination since, in this mode, there is no loss in boiler efficiency (Ref. A-2).

This combination will allow a coal-fired boiler to meet the current NSPS of 300 g/GJ (0.7 lb/10^6 Btu) (Ref. A-6).* On large boilers, it may be difficult to implement combustion modifications without drastically modifying the fuel supply system or reducing the capacity of the system.

*The proposed new NSPS are lower: 260 g/GJ (0.6 lb/10^6 Btu) for coal and 210 g/GJ (0.5 lb/10^6 Btu) for lignite. This combination should be able to meet the new standards as well.

FLUIDIZED BED COMBUSTION

Fluidized bed combustion (FBC) is treated separately because it is a new and unique method of combustion. This approach involves burning coal in a bed of limestone particles fluidized by an air stream which also serves as the source of combustion air. The bed contains about 0.5 wt % coal which is continuously supplied to make up for that consumed by combustion. A typical unit is shown in Figure 5.

The feature of FBC which affects NO_x emissions is the relatively homegeneous temperature of about 843°C (1550°F) which exists throughout the bed. Conventional boilers have a temperature gradient from the flame to the wall with flame temperatures on the order of 1371°C (2500°F). The lower combustion temperature of FBC kinetically inhibits formation of thermal NO_x and, thereby, leads to lower NO_x emissions. FBC is currently being tested on a large scale (30 MWe) test unit and is expected to be available commercially within the next decade (Ref. A-7). Typical NO_x emissions from the development unit range from 86-120 g NO_2/GJ (0.2 - 0.4 lb/10^6 Btu). This emission rate is well under the current NSPS of 300 g NO_2/GJ (0.7 lb/10^6 Btu).* The economics of FBC are not yet well established, and therefore, the cost effectiveness of this approach to NO_x control cannot be assessed.

*The proposed new NSPS are lower: 260 GJ (0.6 lb/10^6 Btu) for coal and 210 g/GJ (0.5 lb/10^6 Btu) for lignite. The emission rate for FBC is well within these emission limits.

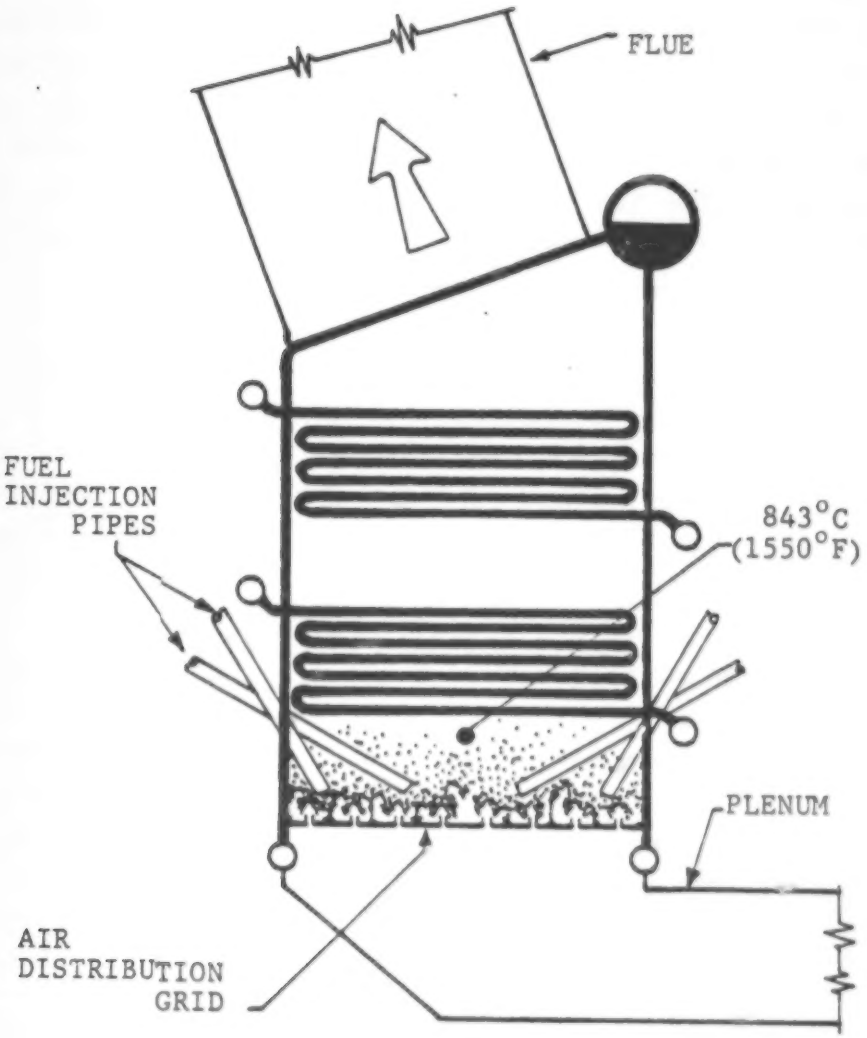


Figure 5. Fluidized Bed Steam Generator.
(Source: Reference A-8)

FLUE GAS TREATMENT (NO_x-ONLY)

Flue gas treatment (FGT) for NO_x control differs from combustion modification in that it involves removal of NO_x after it has been formed rather than by limiting its formation. There are over 20 developers of processes that remove NO_x from flue gas. In addition, there are equivalent numbers of processes available for simultaneous removal of SO_2 and NO_x. These simultaneous SO_2/NO_x processes will be described in a subsequent section.

Essentially all of the feasible NO_x-only FGT processes can be divided into two categories.

- Selective Catalytic Reduction
- Noncatalytic Selective Reduction

In the following sections, both of these process types are discussed with respect to their

- principles of operation,
- status of development,
- operating experiences,
- advantages/disadvantages, and
- costs.

Selective Catalytic Reduction

Selective catalytic reduction (SCR) processes reduce the flue gas NO_x concentration by reacting NO_x with NH_3 according to the following reactions

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

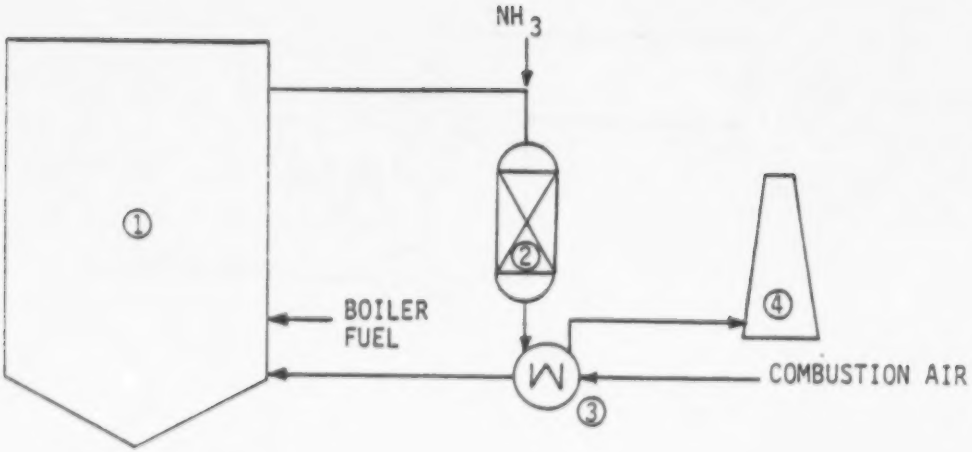
$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

A generalized SCR process flow diagram is shown in Figure 6. In this process, flue gas is injected with NH_3 in an amount equimolar with the NO_x and fed to a catalytic reactor where the NO_x is reduced to N_2. The treated gas is then passed through the combustion air preheater and on to the stack.

The system shown in Figure 6 will work well with gas- or oil-fired units using conventional catalysts and fixed bed reactor designs. With coal firing, potential dust plugging problems dictate the use of one or more of the following approaches:

- operation of the NO_x control system downstream of an efficient and reliable particulate removal device
- a moving bed design which permits the periodic removal of catalyst for cleaning
- a catalyst shape that does not collect the entrained particulates present in the flue gas as they pass through the catalyst bed.

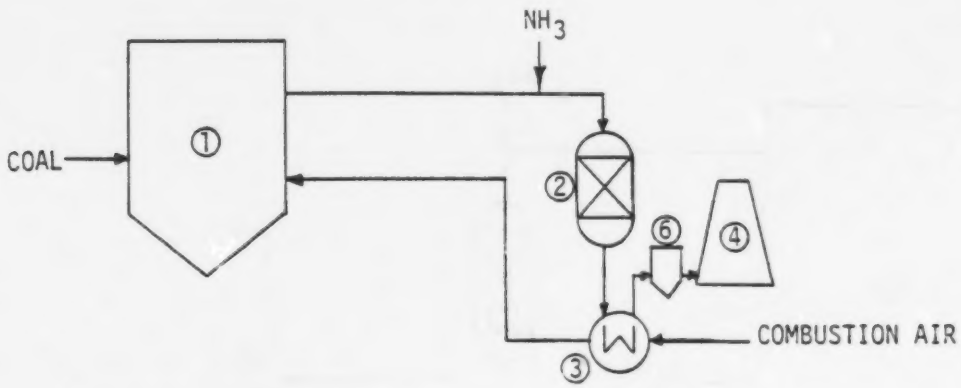
Diagrams which illustrate the process configurations involved in each of these cases are shown in Figure 7.



1. BOILER
2. CATALYTIC REACTOR
3. COMBUSTION AIR PREHEATER
4. STACK

Figure 6. Typical configuration - selective catalytic reduction process for NO_x only.

Option 1. Use of a special catalyst shape that is not affected by flue gas grain loadings



Option 2. Use of a moving bed reaction design which permits the removal of the catalyst for cleaning

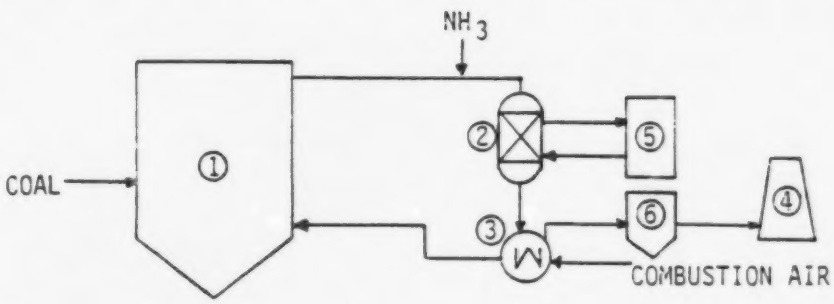


Figure 7. NO_x-only control alternatives involving selective catalytic reduction processes - application to coal-fired boilers.

(Option 3 on next page)

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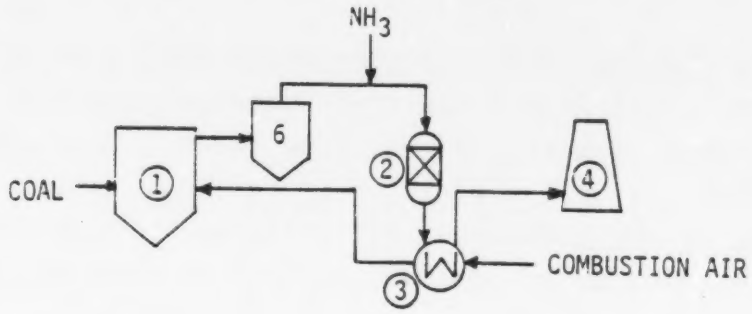
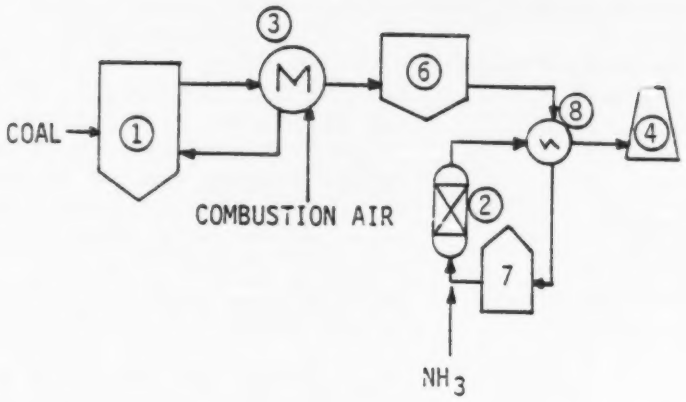
Option 3. Removal of the flue gas particulates upstream of the NO FGT reactor



Option 3a. Use of a "hot-side" ESP



Option 3b. Use of a "cold side" ESP or baghouse

1. Coal fired boiler
2. Catalyic reactor
3. Combustion air preheater
4. Stack
5. Catalyst regeneration system
6. Particulate removal device
7. Heater
8. Feed/product heat exchanger

Figure 7 (Continued)

Of the various configurations which are illustrated in Figure 7, options 1 and 3a are preferred because generally they will have the lowest capital and operating costs. In a retrofit situation, however, it will not always be feasible to install a reactor upstream of the combustion air preheater. This situation may therefore, require an arrangement similar to that shown as option 3b.

The advantages and disadvantages of SCR processes are presented in Table 2.

TABLE 2. ADVANTAGES AND DISADVANTAGES OF SELECTIVE CATALYTIC REDUCTION PROCESSES

Advantages	Disadvantages
Achieves excellent NO_x removal (usually 90% or greater).	May require reheating of the flue gas to attain and control reaction temperature (however, some developmental schemes involve locating the reactor in such a position that reheat may not be required).
Most process-options create no wastes or by-products (except spent catalyst).	Emits NH_3 and under certain conditions, NH_4HSO_4 as a particulate.
Demands lower capital investment and revenue requirements than wet processes.	Some systems are sensitive to particulates and SO_3 in the flue gas.
Involves gas-phase reactions and, therefore, requires less complex operating steps than wet processes.	Difficult to retrofit in some applications.

Source: Reference A-9.

The catalysts used in most SCR processes are oxides of non-noble metals. These have shown the best combination of high reactivity and resistance to SO_x poisoning. Most SCR processes are still in the development stage (<50 MW) although some have been applied commercially. Commercial applications are a recent

occurrence, however some performance data are available on these units. NO_x removals in the 80-90% range and residual NH_3 levels of less than 10 ppm are typical for Japanese installations. A major problem area associated with these processes, however, is the precipitation of NH_4HSO_4 produced by the following reaction

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \qquad (3)$$

The bisulfate forms a liquid precipitate upon formation and decomposes to the reactants when heated. The rate of NH_4HSO_4 formation is a function of reactant concentration and temperature. Precipitation can be avoided if high temperatures are maintained.

While the cost of a specific SCR process will vary depending on a number of site-specific factors, published economic data can be used to develop an expected range of costs. Generally, the capital investment required will range from $15 to $45/kW. Operating costs are similar for the various processes at about 1.5 mills/kWh. These costs are primarily for NH_3 and catalyst which do not change significantly with process type or application. These figures are given in 1976 dollars and are based on a 200-500 MW boiler producing 300 ppm NO_x (Ref. A-10).

Selective Noncatalytic Reduction

Selective noncatalytic reduction, also known as ammonia injection, utilizes the same reaction of NO and NH_3 as does SCR. The major difference is the temperature at which the reaction occurs. Whereas with an SCR process the reaction will proceed at about 400°C (780°F), without a catalyst, a temperature of about 1000°C (1860°F) is required. In this process, NH_3 injection ports are located in the boiler after the combustion zone. A significant control problem with the process is that the reaction is extremely temperature sensitive. A temperature that is 100°C (212°F)

higher or lower can result in increased NO or NH_3 emissions, respectively. The optimum reaction temperature can be lowered by adding H_2 with the NH_3. The process can be controlled therefore by adjusting the H_2 injection rate to respond to temperature changes at the injection point.

Since NH_3 is injected into a high temperature region of the boiler with this process, it is sometimes considered to be a combustion modification technique. However, since its principle of operation is so similar to that of an SCR process, it is discussed here for comparison purposes.

Selective noncatalytic reduction has been reported to give a 70% reduction in NO_x emissions at an NH_3 stoichiometry of 1. Since its demonstration, this process has been installed on a number of Japanese industrial boilers. This process is sensitive to boiler type and configuration with less than ideal configurations giving poorer removals. Advantages and disadvantages of selective noncatalytic reduction processes are presented in Table 3.

TABLE 3. ADVANTAGES AND DISADVANTAGES OF SELECTIVE, NONCATALYTIC REDUCTION PROCESSES

Advantages	Disadvantages
Requires no reheat.	Can achieve only about 60-70% NO_x removal.
Requires no catalyst.	Needs large amounts of reductant (NH_3) in order to achieve high removals; NH_3:NO_x mole ratio greater than 3:1.
Lower capital investments than SCR processes.	Sensitive to temperature variations with potential for significant emissions of NH_3 or NO during boiler load variations.
Generates no liquid or solid waste or by-product streams.	Emits NH_3 and, under certain conditions, NH_4HSO_4 particulate.
Uses homogeneous, gas-phase reactions and, thus, requires the least complicated operating steps of any process.	

Source: Reference A-9.

The operating cost of a typical selective noncatalytic reduction process is reported to be in the range of 0.7 to 1.6 mills/kWh (Ref. A-10). The cost range reported is for a retrofit application and therefore, it is expected that it can be reduced in new boilers if design provisions are made to accommodate the process.

Summary

Comparison of the two process types just discussed indicates that both are capable of controlling power plant NO_x emissions. Selective noncatalytic reduction is the simplest of the two, however it uses large quantities of ammonia. Since ammonia is currently made from natural gas and is in demand as a fertilizer feedstock, its future availability for use in NO_x control may be questionable.

Selection of a particular control technique will depend on the technical and economic factors associated with each specific application. A major problem with all of these processes is that they do not provide any SO_2 removal capability. There are many cases in which SO_2 removal is or will be required in addition to NO_x removal. In these cases, it may not be technically or economically attractive to have an SO_2 removal system installed in series with an NO_x removal system since there are control options available which allow for the simultaneous removal of both SO_2 and NO_x. These processes are discussed in the following section.

SIMULTANEOUS NO_x/SO_2 FLUE GAS TREATMENT

A single process that removes both NO_x and SO_2 may be more economical than using separate processes for NO_x and SO_2 removal. Several FGT techniques for simultaneously removing NO_x and SO_2 from a flue gas stream have been developed in the last few years. These can be divided into two categories: wet and dry. The wet processes utilize a scrubber to absorb the pollutants, whereas the dry processes utilize a combination of adsorption and SCR. As before, the technologies will be discussed with respect to the following items.

- Principle of operation
- Status of development
- Operating experience
- Advantages and disadvantages
- Costs

Wet Processes for NO_x/SO_2 Removal

There are two predominant process types in this category: oxidation-absorption/reduction and direct absorption/reduction. Oxidation-absorption/reduction processes use a gas phase oxidant such as ozone or chlorine dioxide, to convert NO to NO_2. NO_2 and SO_2 are subsequently scrubbed by a circulating sulfite solution. Absorbed NO_2 reacts with the sulfite to form N_2 or N_2O and the absorbed SO_2 reacts with water to form sulfite, thereby replenishing the sulfite solution. The oxidation step is necessary since NO is relatively insoluble in and does not react readily with a sulfite solution. A generalized flow diagram for this process is shown in Figure 8. Prototype scale (10-40 MW) processes of this type have been tested on oil-fired boilers.

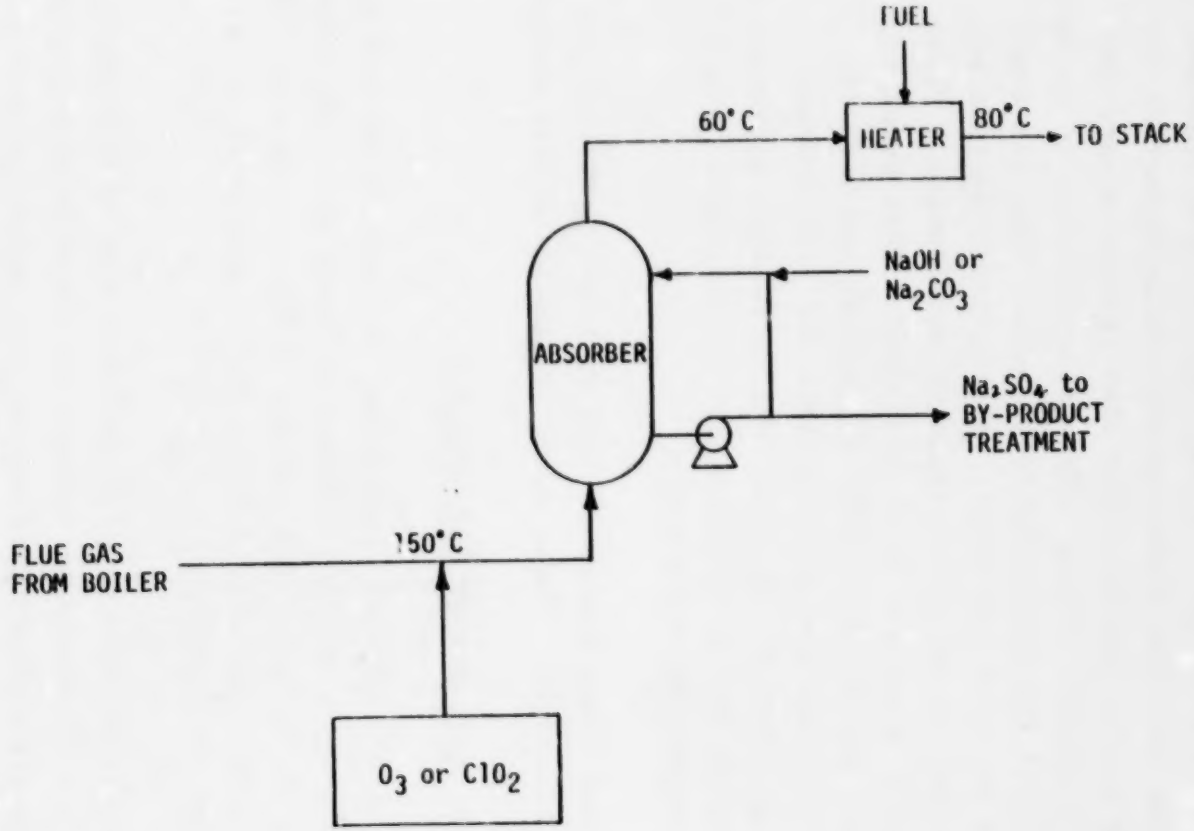


Figure 8. Generalized flow diagram for wet NO_x/SO_2 process.

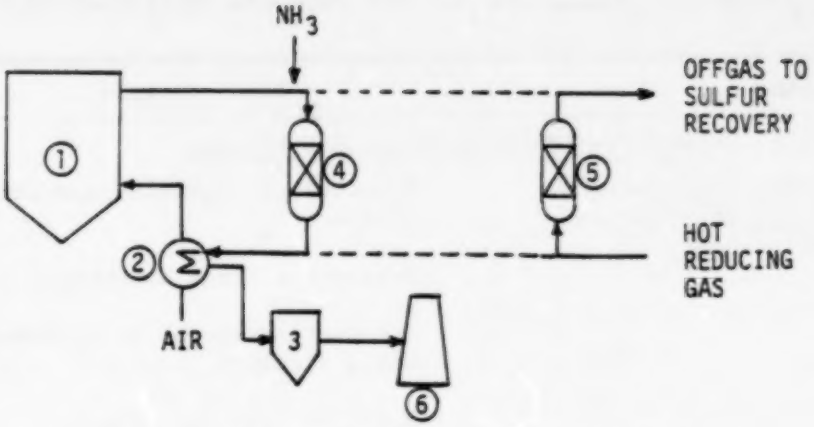
An alternative to the oxidation-absorption/reduction system is one in which NO is absorbed and reduced withour prior oxidation. Processes of this type use an iron chelate complex to facilitate absorption of NO. The absorbed NO is then reduced to N_2 or N_2O by reaction with sulfite. Absorbed SO_2 produces the sulfite used in this reaction. Absorption/reduction processes are less developed than the oxidation-absorption/reduction processes primarily due to the fact that they require a more complex by-product treatment scheme. More specifically, it is very difficult to recover the expensive iron chelate from the spent scrubbing liquor in these processes. Absorption/reduction processes are currently at the pilot scale of development. Plans for prototype scale units are being discussed. Both types of wet processes have exhibited 80-90% NO_x removal and 95+% SO_2 removal. The advantages and disadvantages for both process types are shown in Table 4. An additional potential advantage of the wet processes is that an existing FGD system could be modified to accommodate the NO_x/SO_2 technology.

Costs for these processes vary from $65 to 134/kW and from 4.8 to 8.9 mills/kWh. These costs are based on 1976 dollars.

Dry Processes for NO_x/SO_2 Control

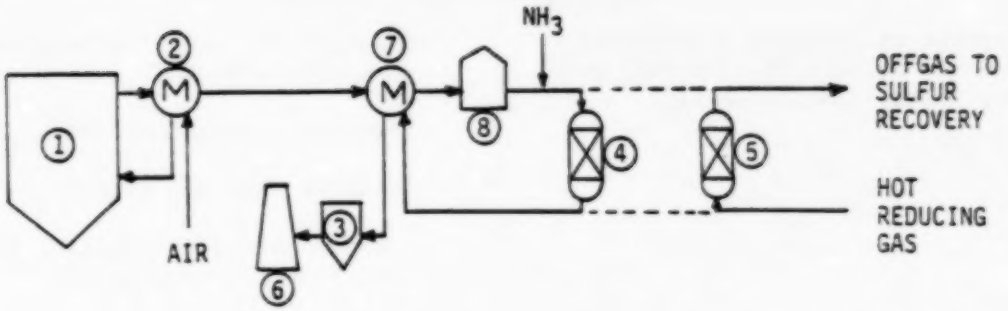
Like the dry NO_x-only processes, the most promising dry process for simultaneous NO_x/SO_2 removal is based upon the reduction of NO_x with NH_3 by SCR. The primary difference is that the copper-based catalyst used functions as an SO_2 adsorbent as well as a NO_x reduction catalyst.

A generalized flow diagram for this type of process is shown in Figure 9. For economic reasons the configuration which involves locating the reactor upstream of the combustion air preheater is favored (flow scheme 9a). However, in a retrofit situa-



9a. "Hot-side" configuration

9b. "Cold side" configuration



1. BOILER
2. COMBUSTION AIR PREHEATER
3. PARTICULATE REMOVEAL SYSTEM(e.g. ESP or baghouse)
4. REACTOR CONTAINING ADSORBENT/SCR CATALYST IN ACCEPTANCE MOLD
5. REACTOR WITH SPENT CATALYST IN REGENERATION MODE
6. STACK
7. FEED/PRODUCT EXCHANGER
8. REACTOR FEED HEATER

Figure 9. Processing scheme used with dry simultaneous NO_x/SO_2 removal system

TABLE 4. ADVANTAGES AND DISADVANTAGES OF WET NO_x/SO_2 PROCESSES RELATIVE TO DRY PROCESS ALTERNATIVES

Advantages	Disadvantages
Oxidation-Absorption/Reduction Systems	
Capable of removing significant amounts of both NO_x (85-90%) and SO_2 (95+%) simultaneously.	Requires an expensive gas-phase oxidant.
	Requires a large absorber.
	Treatment/disposal of blowdown waste streams.
	Requires flue gas reheat.
	Involves a series of complicated processing steps.
	Requires specific ranges of flue gas constituents.
Absorption/Reduction Systems	
Capable of removing significant amounts of both NO_x (85-90%) and SO_2 (95+%) simultaneously.	Requires the use of an expensive chelating compound.
	Requires a large absorber.
	Requires flue gas reheat.
	Complex reaction chemistry and sorbent regeneration scheme.
	Involves a series of complicated processing steps.
	Requires specific ranges of flue gas constituents.

Source: Reference A-9.

tion, this arrangement may not be possible. For this reason, both possible configurations are shown in Figure 9.

The most noteworthy feature of this type of process reactor is the regenerator configuration. In the reactor, SO_2 reacts with CuO and oxygen to form $CuSO_4$. $CuSO_4$ then promotes the NO reduction reaction. Several reactors are operated in "swing" operation, that is, when one reactor is saturated it is taken off line for regeneration and a freshly regenerated reactor is brought on line. The loaded acceptor/catalyst is regenerated by reacting the $CuSO_4$ with a hot reducting gas to produce CuO and SO_2. The regenerator offgas composition will vary depending on the reducing gas used, but, in general, this stream would be sent to a RESOX, modified Claus, liquefaction, or oxidation process for sulfur recovery. Potential products here are H_2SO_4, S, or SO_2.

The NO_x/SO_x version of this process is currently at the pilot-scale level of development. Tests on coal-fired flue gas should begin in the near future as part of an EPA demonstration program. Generally, the advantages and disadvantages are the same as those of the NO_x-only adsorption processes except that the NO_x/SO_2 processes have the additional advantage of removing SO_2 as well as NO_x. Advantages and disadvantages are listed in Table 5.

Costs for this type of process are estimated at 130/kW and 6.0 mills/kWh. Economics vary depending on the characteristics of the flue gas being treated.

Summary

Where simultaneous NO_x/SO_2 removal is required, selection of a particular process will depend almost entirely on the

TABLE 5. ADVANTAGES AND DISADVANTAGES OF THE DRY NO_x/SO_x PROCESS

Advantages	Disadvantages
Capable of removing significant amounts of both NO_x (90%) and SO_x (90%) simultaneously.	Requires use of a reducing gas.
SO_x is converted into a marketable by-product.	Is operationally more complex than throwaway systems.
There are no significant waste streams ($<$10 ppm NH_3 in treated gas).	
Involves gas-phase reactions and, therefore, requires less complex operating steps than wet processes.	
Is not sensitive to particulates.	

specific application. The costs for both wet and dry processes cover the same range and therefore, as a class, the two types of systems are economically competitive. Process selection, then, will depend on how well the particular processes meet the needs of the application.

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